

Guidelines for Integrated Management of Ash Ponds

Volume 2

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Volume 2

1018856

Final Report, July 2009

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This report describes research sponsored by the Electric Power Research Institute (EPRI).

The report is a corporate document that should be cited in the literature in the following manner:

Guidelines for Integrated Management of Ash Ponds: Volume 2. EPRI, Palo Alto, CA: 2009. 1018856.

PRODUCT DESCRIPTION

This report is Volume II of a guidance manual that can be used by coal-fired power plants to help better manage their ash ponds to comply with wastewater regulations. Volume I of this manual (Product 1010123) focused on three of the commonly regulated parameters: total suspended solids (TSS), pH, and ammonia (NH₃). This second volume concentrates on alkalinity, how it is caused and responds in an ash pond, and its impacts on ammonia.

Results and Findings

This manual will help coal-fired power plants understand how to manage the operation of ash ponds to control the discharge of ammonia, TSS, pH, and other parameters of concern. Case studies discussing practices being implemented at operating plants are presented to aid in understanding the mechanisms through which alkalinity is affected and ammonia is removed from ash ponds as well as what can be done to enhance those mechanisms.

Challenges and Objectives

The following are the objectives of Volume II of this manual:

- To deepen the understanding of the relationship between alkalinity, pH, and ammonia treatment through bacterial nitrification and algal uptake
- To identify factors that may impact the ability to meet existing and future discharge limits for these parameters
- To identify the sources of nitrogen species and alkalinity within the facility
- To discuss practices to manage the operation of ash ponds to control ammonia using variables that affect nitrification and algal uptake, such as alkalinity

Applications, Value, and Use

As regulations, operations practices, and pollution control technologies change over time, this report can be used to aid facilities in determining how to best manage their ash ponds to adapt to these changes.

Volume II is focused on alkalinity; additional volumes will be published as necessary to stay up-to-date with changes in regulations, plant operation, and control technologies. Future updates of Volume II may also be published as new technologies and information become available.

EPRI Perspective

Utilities face challenges in managing ash pond chemistry to meet discharge limits. Although careful control of chemical parameters can help utilities meet their goals, the many chemical species present in ponds interact—so the control is not straightforward. This report, combined

with Volume 1 of this series, offers insight, specifically aimed at utility ash ponds, into the chemical relationships among several species and suggests ways to better control the effluent concentrations.

Approach

The information contained in this manual is based on the experience of the investigators, previous studies, and ongoing studies at coal-fired power plants.

Keywords

Ash pond
Ammonia
Alkalinity
pH
Nitrification
Algal assimilation

ABSTRACT

This document is Volume II of a guidance manual that coal-fired power plants can use to help better manage their ash ponds to comply with wastewater regulations. The first volume of this manual (*EPRI Technical Manual: Guidelines for Integrated Management of Ash Ponds, Volume I*. Product 1010123) focused on three of the commonly regulated parameters: total suspended solids (TSS), pH, and ammonia (NH₃). This second volume concentrates on alkalinity and how it influences pH and ammonia assimilation or removal. The purpose of this manual is to accomplish the following:

1. Assist facilities in understanding the existing and future regulatory issues that may affect their discharge of these parameters;
2. Identify plant operating factors that may impact the ability of the facility to meet existing and future discharge limits for these parameters;
3. Identify the sources of these parameters within the facility; and
4. Discuss practices used to manage the operation of ash ponds to control these parameters, including case studies of current practices being implemented by operating plants.

As regulations, operations practices, and pollution control technologies change over the years, this document will also need to evolve and should not be considered a static document. Future updates and additional volumes of this document will be published as necessary to stay up-to-date with changes in regulations, plant operation, and control technologies.

EXECUTIVE SUMMARY

This document is Volume II of a guidance manual that coal-fired power plants can use to help understand the biological, chemical and physical processes taking place in ash ponds and better manage ash ponds to comply with water quality regulations. The material presented within the second volume builds on the material presented within the first volume. The first volume of this manual (Product 1010123) focused on three of the commonly regulated parameters: ammonia (NH_3), TSS, and pH. The second volume focuses on interactions of nitrogen species and the various forms of alkalinity and how these and other factors affect ammonia removal. Later editions of this manual will further develop the management concepts for these parameters as new information becomes available, as well as adding management of other parameters. The first volume of the manual focused on identifying pathways for ammonia removal. The second volume mainly focuses on bacterial nitrification and does not cover in detail other pathways such as algal assimilation.

Ammonia concentrations are increasing in ash ponds, due to increased use and more efficient capture of ammonia in air emission control devices. This can lead to increasing effluent concentrations of ammonia, and failure to meet effluent toxicity limits. Actively managing ammonia removal in ash ponds may be necessary to comply with current or future effluent restrictions. This manual helps to understand how ammonia is used within a power plant, how it and other nitrogen species interact within a power plant and how ammonia is transferred to ash ponds. Ammonia is used for boiler water treatment, selective catalytic reduction (SCR) of NO_x , selective non-catalytic reduction (SNCR) of NO_x , for SO_3 mitigation, and ash conditioning to improve particulate removal efficiency of electrostatic precipitators (ESPs). Flue gas desulfurization (FGD) scrubbers capture ammonia that otherwise would have passed up the stack. Ammonia mainly enters ash ponds with ash sluice water, and FGD purge water if the purge water is added to the pond either before or after treatment.

Ammonia in the effluent of an ash pond is that which is added to the pond from these sources minus that which is assimilated by algae or converted to other nitrogen species by bacterial nitrification. Alkalinity both affects and is affected by bacterial nitrification and algal assimilation. Nitrification and algal assimilation of ammonia both generate acids and consume alkalinity. Algae use sunlight for energy and ammonia nitrogen for growth. Nitrifying bacteria get both energy and nitrogen from oxidizing ammonia, and hence only generate about 1 percent of the mass of new cells as algae for the same amount of ammonia consumed. Algae convert ammonia to cell mass. Nitrifying bacteria convert 99 percent of the ammonia consumed to nitrate, with the remaining converted to cell mass.

Pond pH and alkalinity can be controlled by addition of sodium hydroxide (caustic) to the ash pond. While this can satisfy the alkalinity requirements of nitrifying bacteria, algae require

carbonate alkalinity (for growth), which requires that hydroxide alkalinity be converted to carbonate alkalinity by absorption of CO_2 from the atmosphere.

This volume of the manual introduces a new pond nitrification model that uses information on pond configuration, wind speed, temperature and influent ammonia, alkalinity, and pH to predict monthly effluent parameters. The model can be used to predict the impacts of adding caustic and providing mixing and aeration to improve nitrification performance and affect effluent parameters.

Interactions and effects of algal assimilation and bacterial nitrification are not discussed within this volume in detail as the model is limited to bacterial nitrification. Algal assimilation and bacterial nitrification are each dynamically linked via ash pond dynamics, such as water quality, flow patterns, retention time, and nutrient availability. A management practice, such as aeration, that may be used to enhance one pathway may have consequences for the other.

ACRONYMS AND ABBREVIATIONS

° C	degrees Celsius
° F	degrees Fahrenheit
Al	aluminum
AOB	ammonia oxidizing bacteria
C	carbon
Ca	calcium
CaCO ₃	calcium carbonate
cfm	cubic feet per minute
cm	centimeter
CO ₂	carbon dioxide
CO ₃ ⁻²	carbonate
DO	dissolved oxygen
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
Fe	iron
ft	foot
FGD	flue gas desulfurization
H	hydrogen
H ⁺	hydrogen ion
HCO ₃ ⁻	bicarbonate
H ₂ CO ₃	carbonic acid
hp	horsepower
H ₂ SO ₄	sulfuric acid
HRT	hydraulic residence time
K	potassium
L	liter
lbs	pounds
mg	milligram
Mg	magnesium
mg/L	milligrams per liter

mgd	million gallons per day
mm	millimeters
mM	millimoles
MW	megawatt
N	nitrogen
N ₂	nitrogen gas
Na	sodium
NaOH	sodium hydroxide
(NH ₂) ₂ CO	urea
NH ₃	ammonia (un-ionized)
NH ₃ -N	ammonia quantified as nitrogen
NH ₄ ⁺	ammonium ion
NO	nitrogen monoxide
NO ₂	nitrogen dioxide
NO ₂ ⁻	nitrite
NO ₃ ⁻	nitrate
N ₂ O	nitrous oxide
NO _x	nitrogen oxides
NOB	nitrate oxidizing bacteria
O	oxygen
O ₂	oxygen gas
OH ⁻	hydroxide
P	phosphorus
pK _A	acidity constant
ppm _v	parts per million by volume
ppm _w	parts per million by weight
RMP	Risk Management Plan
S	sulfur
SCR	selective catalytic reduction
Si	silicon
SNCR	selective non-catalytic reduction
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
Ti	titanium
TKN	total Kjeldahl nitrogen
TSS	total suspended solids
USEPA	U.S. Environmental Protection Agency

CONTENTS

1 INTRODUCTION	1-1
2 NITROGEN CYCLE IN COAL-FIRED POWER PLANTS	2-1
Nitrogen Uses and Sources in a Power Plant	2-1
Common Nitrogen Species Present in a Power Plant	2-1
Combustion Byproducts	2-2
Reduction of NO _x	2-3
Opacity Mitigation	2-5
Ash Conditioning	2-6
Flue Gas Desulfurization (FGD) Systems	2-6
Nitrogen Cycle in an Ash Pond	2-7
Algal Assimilation of Nitrogen	2-7
Bacterial Nitrification	2-8
3 ALKALINITY	3-1
Carbonate Species and Alkalinity	3-1
Non-Carbonate Alkalinity	3-7
Sources of Alkalinity (or Acidity) in Ash Ponds	3-8
Coal Combustion	3-8
SO ₃ Mitigation	3-10
Ash Conditioning	3-11
FGD Systems	3-11
Other Plant Operations Impacting Alkalinity	3-13
Caustic Addition to Control Pond Effluent pH	3-13
4 ROLE OF ALKALINITY IN AMMONIA REMOVAL	4-1
Alkalinity in Algal Assimilation of Nitrogen	4-1
Alkalinity in Bacterial Nitrification	4-2

Summary	4-4
5 ASH POND MANAGEMENT METHODS FOR EFFECTIVE AMMONIA REMOVAL	5-1
Effect of Temperature on Nitrifier Growth Rate	5-2
Effect of pH on Nitrifier Growth Rate	5-3
Effect of Ammonia Concentration on Nitrifier Growth Rate	5-3
Effect of Dissolved Oxygen Concentration on Nitrifier Growth Rate	5-4
Field Methods Used for Managing Nitrification.....	5-5
Case Study – Using a Predictive Tool.....	5-5
Adding Caustic to Increase Alkalinity	5-6
Mixing to Increase Residence Time	5-8
Increasing Oxygen Transfer	5-9
Model Benefits.....	5-10
6 REFERENCES	6-1

LIST OF FIGURES

Figure 2-1 Nitrogen Species Within a Power Plant.....	2-2
Figure 2-2 Selective Catalytic Reduction Process	2-3
Figure 2-3 Selective Non-catalytic Reduction Process	2-4
Figure 2-4 Example of “Blue Plume” Stack Emissions	2-5
Figure 2-5 Nitrogen Cycle in an Ash Pond.....	2-7
Figure 3-1 Carbonate Species as a Function of pH (total Carbonates = 100 mg/L)	3-2
Figure 3-2 Acid Titration (Total Carbonates = 100 mg/L).....	3-3
Figure 3-3 Phenolphthalein Indicator Dye Color Change at pH 8.3.....	3-4
Figure 3-4 Methyl Orange Dye Color Change at pH 4.3.....	3-4
Figure 3-5 Hydroxide and Carbonate Species as a Function of pH (total Carbonates = 100 mg/L)	3-5
Figure 3-6 Acid Titration (Total Carbonates = 100 mg/L, pH =11)	3-6
Figure 3-7 Acidity Titration Curves for FGD Wastewater for Three Power Plants	3-12
Figure 5-1 Nitrifier Maximum Specific Growth Rate as a Function of Temperature.....	5-2
Figure 5-2 pH-Specific Nitrifier Growth Rate as a Function of pH.....	5-3
Figure 5-3 Ammonia-Specific Nitrifier Growth Rate as a Function of Ammonia Concentration and Temperature	5-4
Figure 5-4 DO-Specific Nitrifier Growth Rate as a Function of DO Concentration.....	5-5
Figure 5-5 Effects of Adding Caustic to Improve Ammonia Removal in Model Ash Pond	5-7
Figure 5-6 Effects on Ammonia Removal of Manipulating Residence Time within an Ash Pond.....	5-9
Figure 5-7 Effects on Ammonia Removal of Manipulating Dissolved Oxygen Levels by Aeration within an Ash Pond	5-10

LIST OF TABLES

Table 2-1 Oxidation States of Common Nitrogen Species Within a Power Plant	2-1
Table 3-1 Acidity Constants for Carbonates	3-2
Table 3-2 Acidity Constants for Ammonia and Other Anions.....	3-7
Table 3-3 Selected Chemical Properties of Fly Ash Samples[7]	3-9
Table 3-4 Data on Alkalinity, Acidity and pH of FGD Wastewater [6]	3-12
Table 4-1 Comparison of Requirements for Algal Assimilation and Bacterial Nitrification	4-3
Table 5-1 Model Input Parameters for Case Study.....	5-6
Table 5-2 Caustic Addition Within an Ash Pond for Model Simulation	5-8

1

INTRODUCTION

Historically, ash ponds at steam electric power plants have been primarily designed, operated, and managed to provide sufficient area and volume for sedimentation and long-term storage of coal fly ash and bottom ash, and to meet historical categorical effluent limitations for pH and total suspended solids (TSS). The location of an ash pond was selected to provide as much ash storage capacity as possible with little consideration for future changes in wastewater regulations and requirements.

As wastewater regulations have evolved throughout the years, and as new contaminants are introduced through power plant operations, the concept that ash ponds are simply facilities for storing ash is no longer applicable. New, pending, and future regulations will require that existing ash ponds be actively operated and managed to achieve new discharge limits set by the regulations. When new ash ponds are needed at an existing power plant, the design and construction of the new pond(s) must take into account the need for wastewater treatment to remove more than just TSS, i.e., ash. Only dry ash handling is permitted for new power plants.

This document has been developed as the second volume of a guidance manual that coal-fired power plants can use to help better manage their ash ponds to comply with wastewater regulations. Volume I of this manual was published in March 2006 [1]. Since regulations, plant operations, and pollution control technologies will continue to evolve, this manual will also evolve and should not be considered a static document. Future updates and additional volumes of this document will be published as necessary to stay up-to-date with changes in the regulations, plant operations, and control technologies.

This first volume of this manual focused on three of the commonly regulated parameters: ammonia (NH_3), TSS, and pH. The second volume focuses on nitrogen and alkalinity contributions and alkalinity's effects on ammonia removal in ash ponds. Later editions of this manual will further develop the management concepts for these parameters as new information becomes available, as well as adding management of other parameters. The purpose of this manual is to:

1. Assist facilities in understanding the existing and future regulatory issues that may affect their discharge of these parameters;
2. Identify plant operating factors that may impact the ability of the facility to meet existing and future discharge limits for these parameters;
3. Identify the sources of these parameters within the facility; and
4. Discuss practices used to manage the operation of ash ponds to control these parameters, including case studies of current practices being implemented by operating plants.

This report is broken into the following chapters:

- Chapter 1: Introduction – This chapter summarizes the purpose of this manual.
- Chapter 2: Nitrogen Cycle in Coal-Fired Power Plants – This chapter outlines various nitrogen species and their uses and interactions within a power plant. Sources of nitrogen species to ash ponds and their subsequent transformation within the pond due to biological processes are summarized. Ammonia removal from ash ponds can be better managed by understanding the nitrogen species within a power plant and how ammonia is ultimately transferred to ash ponds.
- Chapter 3: Alkalinity – This chapter includes a summary of carbonate and non-carbonate alkalinity found within a coal-fired plant and processes within power plants that contribute to alkalinity or acidity within ash ponds.
- Chapter 4: Role of Alkalinity in Ammonia Removal – The role of alkalinity in both algal assimilation and bacterial nitrification is summarized, and the assimilation and nitrification processes are compared based on ammonia removal. This subject has not been extensively studied in ash ponds and this chapter provides a basis for future research.
- Chapter 5: Ash Pond Management Methods for Effective Ammonia Removal – This chapter is devoted to adjusting residence time, aeration, and caustic addition to manipulate ash ponds for effective ammonia removal. Cost savings may be realized when a balance between nitrification and algal assimilation can be maintained within an ash pond.
- Chapter 6: References – List of works cited in this document.

2

NITROGEN CYCLE IN COAL-FIRED POWER PLANTS

The purpose of this chapter is to describe the various species of nitrogen compounds in coal-fired power plant ash ponds, and how these species are transformed in ash ponds.

Nitrogen Uses and Sources in a Power Plant

Common Nitrogen Species Present in a Power Plant

Nitrogen is present in a coal-fired power plant in multiple oxidation states, ranging from +5 to -3, with +5 being the most chemically oxidized form, and -3 being reduced. Oxidation states of various species used or produced are shown in Table 2-1.

Table 2-1
Oxidation States of Common Nitrogen Species Within a Power Plant

Chemical Name	Medium	Chemical Formula	Oxidation State
Nitrate	Water	NO_3^-	+5
Nitrogen dioxide	Air	NO_2	+4
Nitrite	Water	NO_2^-	+3
Nitric Oxide	Air	NO	+2
Nitrous Oxide	Air	N_2O	+1
Nitrogen Gas	Air	N_2	0
Ammonia	Water	NH_3	-3
Ammonium	Water	NH_4^+	-3
Urea	Liquid Chemical	$(\text{NH}_2)_2\text{CO}$	-3

Note: Nitrogen is also present within coal, whose chemical formula can be approximated as $\text{C}_{137}\text{H}_{97}\text{O}_9\text{NS}$.

Figure 2-1 illustrates the various potential sources and uses of nitrogen within a power plant and how nitrogen is commonly transformed in water and air streams throughout the plant. Processes within a power plant that may use or produce or process nitrogen species include coal combustion, selective catalytic reduction (SCR)/selective non-catalytic reduction (SNCR), ammonia injection for opacity (blue plume) mitigation, ash conditioning, and flue gas desulfurization (FGD). These processes can ultimately contribute to sources of nitrogen species within ash ponds, and are discussed further in the following chapters.

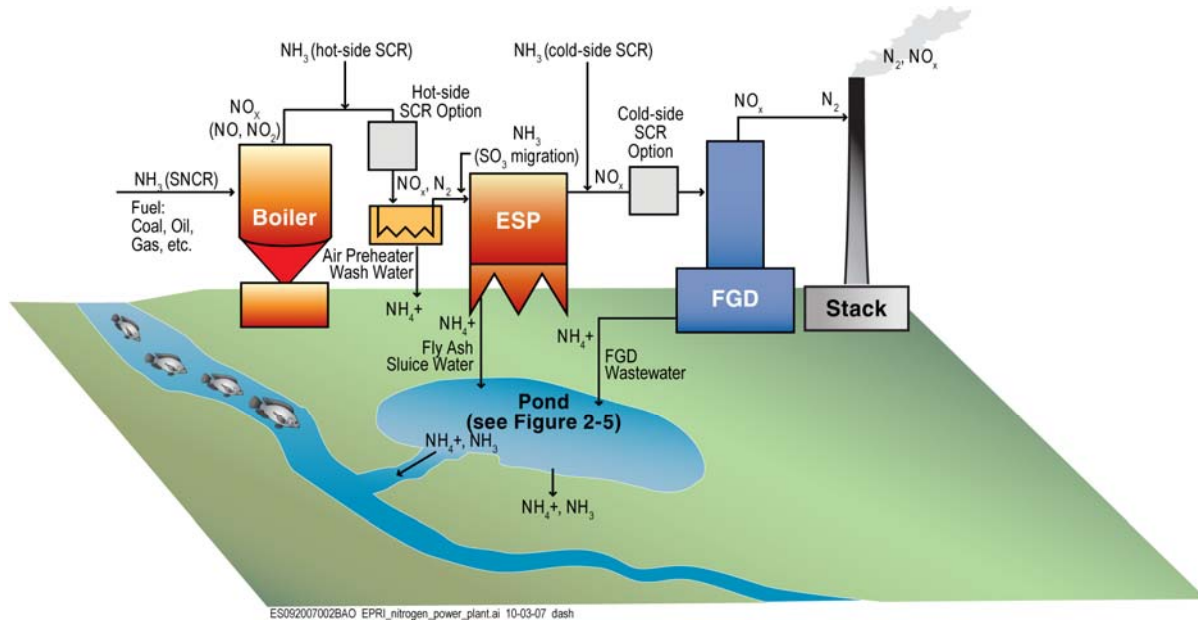


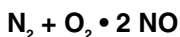
Figure 2-1
Nitrogen Species Within a Power Plant

Combustion Byproducts

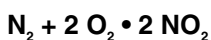
Coal-fired power plants generate electricity predominately by the combustion of carbon present in coal with atmospheric oxygen. The generation of various oxides of nitrogen results from the combustion of nitrogen present in both coal and combustion air, and atmospheric oxygen. These oxides of nitrogen, mainly nitric oxide (NO) and nitrogen dioxide (NO₂), are collectively referred to as NO_x.

NO_x reacts with atmospheric oxygen to produce ground-level ozone, nitrate (NO₃⁻) particles, and nitric acid aerosols, which adversely affect the respiratory system. Nitric acid can affect visibility, and is one source of acid rain, which affects lakes with low buffering capacity. In addition to causing acidification of lakes with low buffering capacity, nitric acid deposition in rainfall contributes a nitrogen load to water bodies, increasing eutrophication.

The two principal sources of NO_x in coal-fired power plants are thermal NO_x and fuel NO_x. Thermal NO_x is formed as a result of the oxidation of diatomic nitrogen (N₂) found in combustion air (Equations 2-1 and 2-2) and is a function of the temperature and the residence time of the nitrogen at that temperature; the higher the temperature of the flame and the residence time, the higher the formation of thermal NO_x. Thermal NO_x is usually formed above 2,200° F.

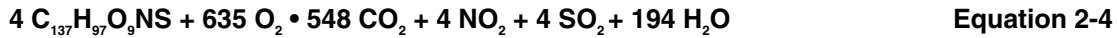


Equation 2-1



Equation 2-2

Fuel NO_x is formed when the nitrogen in fuels combines with the excess oxygen in the air. Combustion equations for bituminous coal are shown in Equations 2-3 and 2-4. Thus each ton of bituminous coal burned produces about 15 pounds of fuel NO_x -N.



Reduction of NO_x

Two processes are typically used to remove NO_x from coal-fired boilers: selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). Both SCR and SNCR systems use ammonia to react with NO_x , which produces nitrogen gas and water.

SCR is a process wherein ammonia (NH_3) is injected into the flue gas ahead of a catalyst bed, where the injected ammonia reacts with NO_x (Equation 2-5).



Figure 2-2 shows the SCR process. This process may take place at anywhere between 500° F and 1,200° F depending on the catalyst used. SCR can reduce NO_x emissions by up to 90%. As the catalyst is used, it becomes less effective at promoting the reaction of ammonia with NO_x , and excess ammonia is required to achieve the emission controls required.

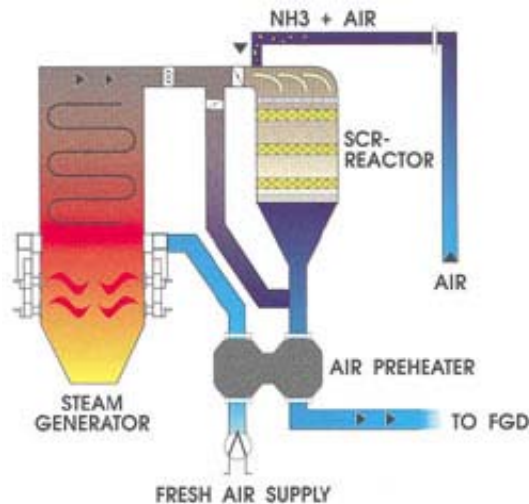


Figure 2-2
Selective Catalytic Reduction Process

Source: Hamon Research-Cottrell, Inc. [2]

In SNCR systems, ammonia or urea is injected into the flue gas hot-side of the boiler (see Figure 2-3) where the temperature is high enough (approximately 1,400-1,600° F) to drive the reaction of ammonia with NO_x to form N_2 . SNCR uses the higher temperature of the furnace and

holdup time in the flue to react ammonia with NO_x without the use of catalysts. Reactions are the same as with SCR (Equation 2-5 above). SNCR can reduce NO_x emissions by 70%.

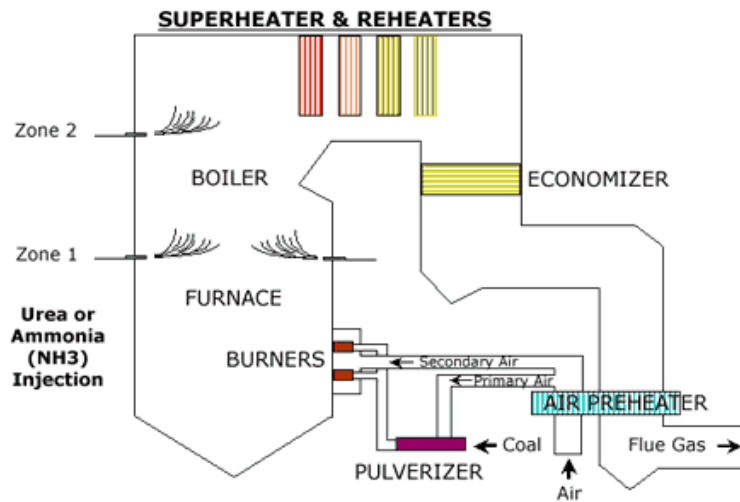


Figure 2-3
Selective Non-catalytic Reduction Process

Source: Hamon Research-Cottrell, Inc. [3]

Storing ammonia on site can trigger the need for the preparation of a Risk Management Plan (RMP). Therefore, some plants that use ammonia in SCR or SNCR produce ammonia on-site from urea. Urea ($[\text{NH}_2]_2\text{CO}$) is converted to ammonia and carbon dioxide (CO_2) by reacting it with water (Equation 2-6).



Reactions of ammonia with NO and NO_2 are shown as Equations 2-7 and 2-8.



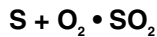
The reaction of ammonia with NO_x in both SCR and SNCR requires an excess of ammonia, referred to as “ammonia slip.” The ammonia slip for an SCR system can range from less than 1 part per million by volume (ppm_v) to 20 ppm_v . As the SCR catalyst ages, its activity decreases, and the ammonia slip increases. Typical ammonia slip values from operating SCR systems are generally in the 0 to 2 ppm_v range. The ammonia slip for SNCR systems is higher than with SCR systems, ranging from about 5 ppm_v to greater than 25 ppm_v . Typical ammonia slip values from operating SNCR facilities are generally in the 5 to 10 ppm_v range.

This ammonia is usually adsorbed on fly ash and removed with the fly ash. When fly ash is sluiced with water for transport to the ash pond, most of this ammonia dissolves in the sluice water. At typical ammonia slip values, concentrations of ammonia on dry fly ash range from less than 50 parts per million by weight (ppm_w) to over 500 ppm_w [1]. When the fly ash is wet-sluided,

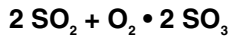
the adsorbed ammonia is released into the sluice water and subsequently discharged to the ash pond. If a fly ash with an ammonia concentration of 100 ppm_w is wet-slucied producing a slurry with 5% ash, the ammonia concentration in the sluice water will be 5 milligrams per liter (mg/L), assuming all ammonia is released to the water, and there is no volatilization of the ammonia.

Opacity Mitigation

Production of sulfur trioxide (SO₃) is becoming a greater concern in power plants due to the potential impacts on plant emissions and plant operation and maintenance. During combustion the organic sulfur and pyrites (ferrous sulfide) present in coal result in the generation of SO_x or oxides of sulfur (Equations 2-9 and 2-10).

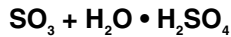


Equation 2-9



Equation 2-10

Of the two species, sulfur dioxide (SO₂) predominates. Use of catalytic reduction for NO_x control increases SO₂ conversion to SO₃. The SO₃ reacts with water vapor to produce a sulfuric acid (H₂SO₄) mist or “blue plume” (Equation 2-11) that can violate opacity emissions requirements and therefore requires treatment. Figure 2-4 shows a bluish plume being emitted from a stack during SCR/SNCR season.



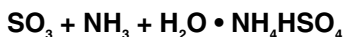
Equation 2-11



Figure 2-4
Example of “Blue Plume” Stack Emissions

Source: Schulz and Smyrniotis, 2005 [4]

The opacity can be mitigated by adding ammonia to the gas stream containing SO_3 , which results in the formation of ammonium bisulfate (Equation 2-12).



Equation 2-12

The amount of ammonia added for SO_3 mitigation is dependent on the SO_3 concentration. Higher-sulfur coals will need more ammonia feed. Ammonia addition for SO_3 mitigation is typically near 10 ppm_v and can range up to 25 ppm_v, which for a 1,000-megawatt (MW) plant at 3,500 cubic feet per minute (cfm) per MW is approximately 2,200 to 5,600 pounds (lbs) per day of ammonia.

Ammonium bisulfate is a sticky solid that is then removed by particulate emissions control devices such as electrostatic precipitators (ESPs). The resulting fly ash contains ammonium bisulfate. When this fly ash is sluiced with water, the ammonium bisulfate is converted to ammonium ions and partially neutralized sulfuric acid (Equation 2-13).



Equation 2-13

Ash Conditioning

Flue gas particulate removal is often accomplished using an electrostatic precipitator. Particulate removal is based on giving the particles a surface charge, and the charged particles are attracted to collecting plates of opposite charge. The plates are vibrated to remove the particles, which fall into a hopper. Efficiency of particle removal depends on the electrical conductivity of the ash particles. When removal efficiency is adversely affected by low ash conductivity (most often caused by burning low-sulfur coal), removal efficiency can be increased by chemically conditioning the ash. Ammonia is one option used for this conditioning. The mechanisms of conditioning were described in Chapter 2 of Volume I of this manual [1]. Ammonia is injected into the flue gas prior to the ESP to condition the fly ash. If the fly ash is removed by wet-sluicing, the ammonia dissolves in the sluice water which is subsequently discharged to the ash pond. Ammonia addition for ash conditioning at one typical plant is 2-4 ppm_v ammonia in the air stream. Assuming the majority is captured in the ESP and sluiced to the ash pond, at a 1,000-MW plant with 3,500 cfm per MW, this equates to 450 to 900 lbs/day of ammonia.

Flue Gas Desulfurization (FGD) Systems

Nitrogen species are not added or produced in FGD reactions. However, FGD scrubbers can capture ammonia that is in the flue gas from the other processes, which passes through particulate control devices. As a result, blowdown from FGD systems can contain appreciable concentrations of ammonia and nitrates. If FGD blowdown is discharged to an ash pond after solids removal or other treatment processes, this stream may contribute significant amounts of nitrogen to the ponds. Based on a limited number of samples collected as part of previous studies, total Kjeldahl nitrogen (TKN) ranges from 2 to 80 mg/L in FGD blowdown [6]. A plant with 0.5 million gallons per day (mgd) of FGD blowdown would have a contribution of approximately 8 to 330 lbs/day of ammonia as nitrogen ($\text{NH}_3\text{-N}$), at this concentration range.

Nitrogen Cycle in an Ash Pond

As discussed in the previous chapter, the principal forms of nitrogen entering an ash pond are ammonia and nitrate. Ammonia enters the pond with ash sluice water. Due to its high solubility, ammonia rapidly dissolves from the ash. Ammonia in the pond can be removed by one of three mechanisms:

- It can remain unchanged and leave the pond in the outflow.
- It can be assimilated by algae and used to grow additional algal mass.
- It can be transformed by bacterial nitrification to nitrite and then to nitrate.

Figure 2-5 summarizes the major processes affecting nitrogen within an ash pond. Algal assimilation of ammonia and bacterial nitrification of ammonia are further discussed in the first volume of this manual.

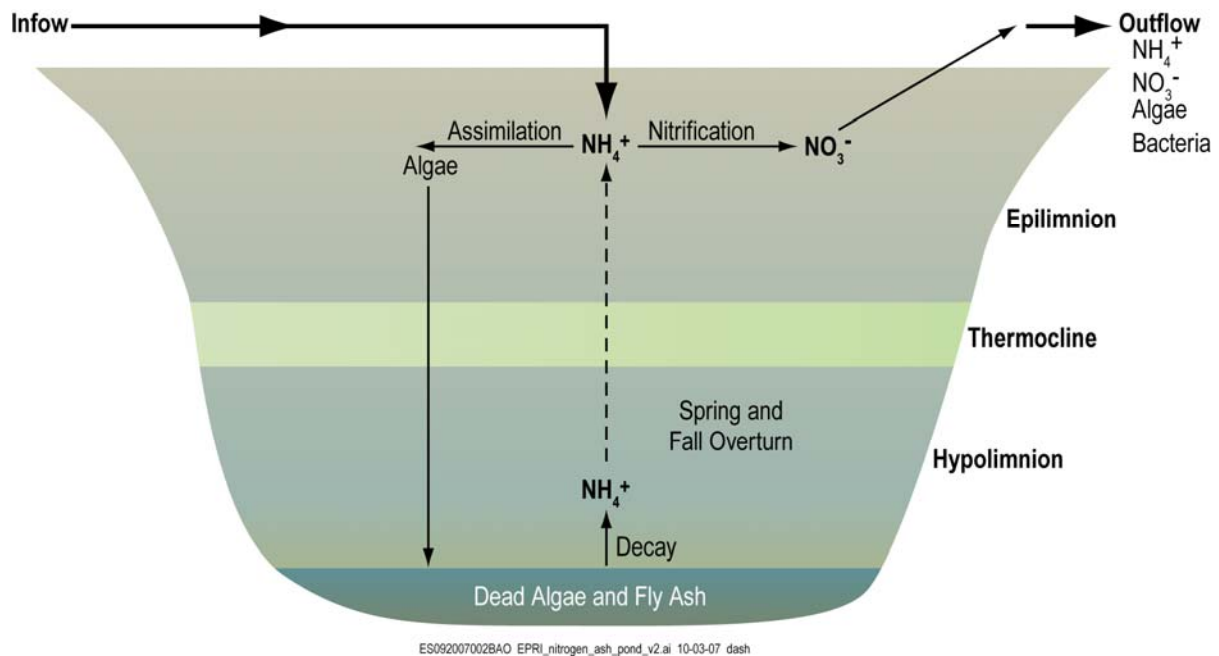


Figure 2-5
Nitrogen Cycle in an Ash Pond

Algal Assimilation of Nitrogen

A typical algal cell is assumed to have a chemical composition of $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$, which, on a dry mass basis, is approximately 36% carbon (C), 7.4% hydrogen (H), 50% oxygen (O), 6% nitrogen (N), and 1% phosphorus (P). In the presence of sunlight, algae use photosynthesis to synthesize their own food (glucose). The glucose is then used to produce other organic compounds needed by the cells for growth, and used as a fuel for other cellular functions.

Both photosynthesis and respiration occur during daylight, with only respiration occurring after daylight. The rate of photosynthesis far exceeds the respiration rate, resulting in a net increase of oxygen during the daylight. During the photosynthesis and respiration processes, the algae will also absorb N, P, and other trace nutrients needed to build new cell matter and sustain cell functions. Based on the typical composition of algae, $C_{106}H_{263}O_{110}N_{16}P$, 6.3 mg/L of nitrogen is required to produce 100 mg/L of new algal mass, or approximately 15.9 lbs of algae per 1.0 lbs of nitrogen. Ammonia is the easiest form of nitrogen for uptake and assimilation by algae and it will be preferentially consumed from the water column for production of new biomass, with nitrate being preferred next.

Addition of ammonia to an ash pond in spring can result in a significant growth or “bloom” of algae. At night, algal respiration of oxygen can exceed the capacity of the oxygen transfer capacity of the pond surface, resulting in a die-off of the algae. The dead algae either settle to the bottom of the pond or flow out of the pond outlet, resulting in increased TSS of the discharge. The algae that settle to the bottom of the pond subsequently decay, releasing the ammonia that was assimilated by the algae. When the pond is stratified, the ammonia may remain at the lower stratum (hypolimnion), and subsequently be released to the shallower stratum (epilimnion) during spring and fall overturns. Algal assimilation may be limited by phosphorus availability within an ash pond as well as availability of other nutrients. This was discussed in more detail in Volume I.

Bacterial Nitrification

Certain bacteria use ammonia as their sole energy source. This process is called nitrification and is the conversion of ammonia-nitrogen to nitrate-nitrogen. The conversion occurs in two steps, with each step being mediated by different genera of bacteria. The first step involves the conversion of ammonium to nitrite, which is mediated by ammonia oxidizing bacteria (AOB—historically considered to be only the genus *Nitrosomonas* but now recognized to potentially represent a wider range of genera)[1]. The second step is the conversion of nitrite to nitrate, which is mediated by nitrite oxidizing bacteria (NOB – historically considered to be only the genus *Nitrobacter* but now recognized to potentially represent a wider range of genera). These two steps result in an overall nitrification reaction given by Equation 2-14:



Equation 2-14

The theoretical oxygen requirement for nitrification can be computed from this equation. Two moles of oxygen gas (O_2) are required to oxidize 1 mole of NH_4^+-N . On a mass basis, this is equivalent to 4.57 lbs of O_2 to oxidize 1.0 lbs of NH_4^+-N .

The energy yield from the nitrification process is primarily used by the bacteria for metabolic processes and only a small amount of the ammonia is used to produce new cell matter. Simultaneously with nitrification, the bacteria use the energy, ammonium, oxygen, inorganic carbon, and other nutrients to generate new cell mass. For each pound of ammonia nitrogen that is consumed, 0.17 lbs of bacterial cells are produced. For a pond influent of 10 mg/L $\text{NH}_4^+\text{-N}$, the pond would reach an equilibrium concentration of 1.7 mg/L of nitrifying bacteria, if the ammonia is completely consumed by nitrification. This is in contrast to algal assimilation of ammonia that would generate 159 mg/L of algae cells for the same influent ammonia concentration.

3

ALKALINITY

Alkalinity is broadly defined as the capacity of water to neutralize acids (i.e., to absorb hydrogen ions without significant pH change). It should not be confused with pH. The principal alkaline ions consist of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide (OH^-) as well as species such as un-ionized ammonia, silicates, borates, phosphates, and organic bases. A water sample may contain high alkalinity at neutral or even acidic pH, or can have low alkalinity at a pH well above 7. It should be thought of as equivalent to buffering or resistance to change in pH when acid is added. This chapter introduces the concept of alkalinity and describes sources of alkalinity in ash ponds.

The role of alkalinity in algal uptake and bacterial nitrification of ammonia is described in Section 4.

Carbonate Species and Alkalinity

In natural water, alkalinity is the result of carbonate and bicarbonate (collectively referred to as carbonates) ions in solution and as a result alkalinity is reported as mg/L as calcium carbonate (CaCO_3). Calcium carbonate reacts with acid in two reactions (Equations 3-1 and 3-2) to produce carbonic acid (H_2CO_3).



The molecular weight of CaCO_3 is 100. Therefore, 1 millimole (mM) of calcium carbonate is 100 mg/L and will consume 2 mM of acid (H^+). Alkalinity is reported as CaCO_3 but is normally present as carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). The two-step reaction of carbonate to carbonic acid is shown as Equations 3-3 and 3-4.



These reactions take place around set pH values, referred to as acidity constants (pK_A) (see Table 3-1).

When the pH is above the pK_A the majority of the carbonate is present in the alkaline form (CO_3^{2-}) and will react with the acid (H^+) ion. When the pH is below the pK_A , the majority of the carbonate is present in the acidic form (for the first pK_A this is HCO_3^- , for the second is H_2CO_3).

Table 3-1
Acidity Constants for Carbonates

Reaction	pK _A
$\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$	10.3
$\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$	6.3

The relationship of the three (CO_3^{2-} , HCO_3^- , and H_2CO_3) carbonate species (assuming that the total carbonates is 100 mg/L as CaCO_3) is shown as Figure 3-1. Above pH 10.3, carbonate is the principal form of the three species. Carbonate and bicarbonate are equal at pH 10.3 (the first pK_A). At pH 8.3, the predominant species is bicarbonate and little carbonate or carbonic acid is present. Bicarbonate and carbonic acid are equal at pH 6.3. Below this pH carbonic acid predominates. To change the pH from the alkaline side of the pK_A, acid is consumed.

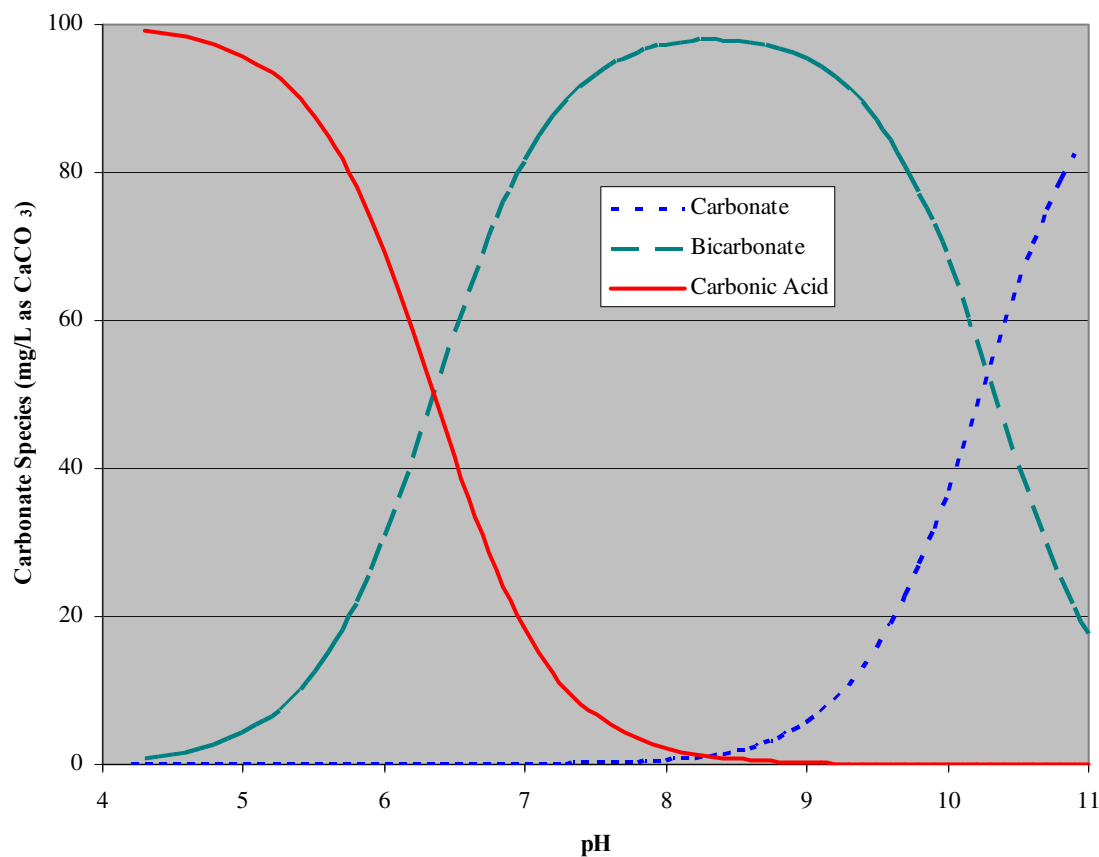


Figure 3-1
Carbonate Species as a Function of pH (total Carbonates = 100 mg/L)

An alkalinity titration is performed to determine the amount and forms of the carbonate species by adding acid to an alkaline sample. Figure 3-2 illustrates what happens when a water sample containing 100 mg/L of carbonates (as CaCO_3) at pH 11, in which little bicarbonate or carbonic acid is present (i.e., pH 11 is much greater than 10.3), is titrated with acid (note acid addition

from right to left in the diagram). This example does not take into account hydroxide, which is present in significant concentration at pH above 10.

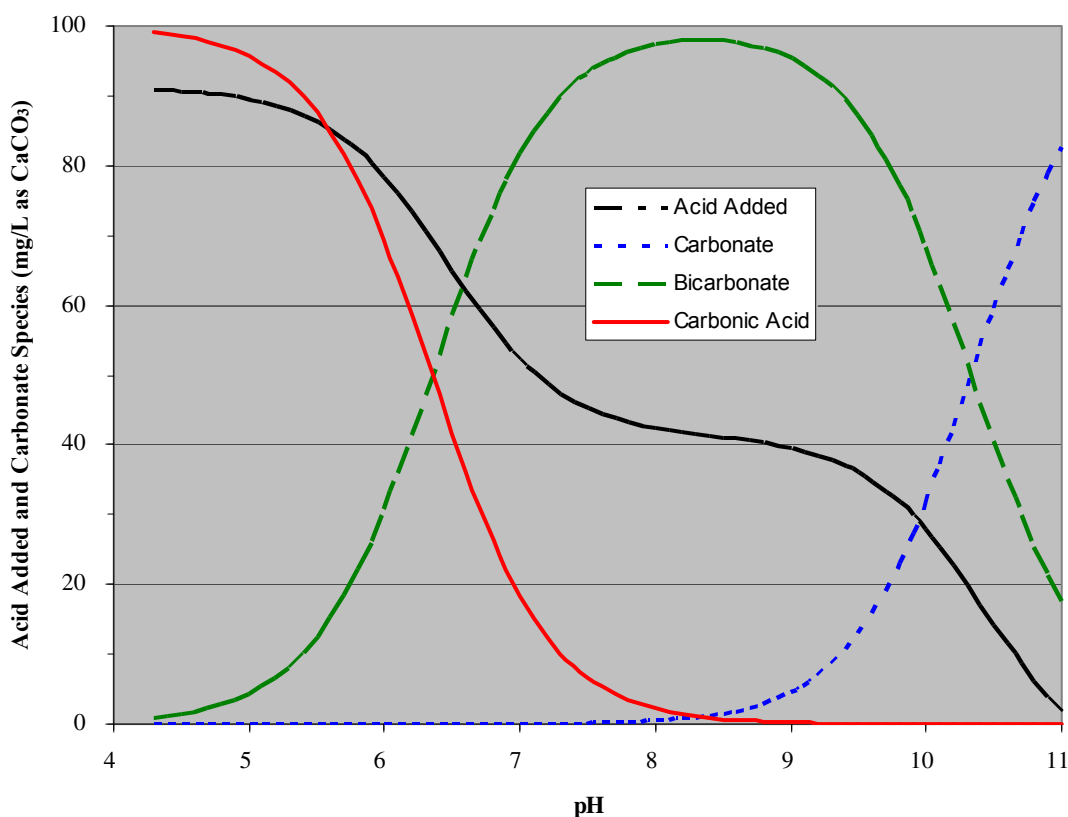


Figure 3-2
Acid Titration (Total Carbonates = 100 mg/L)

The initial pH in this illustration is 11. At this pH 80 percent of the total carbonates is present as carbonate, and 20 percent as bicarbonate. As acid is added (read from right to left) pH is lowered and carbonate is converted to bicarbonate. As pH approaches the pK_a of 10.3, it takes more acid to produce a change in pH, due to the acid being consumed in the conversion of carbonate to bicarbonate. This resistance to pH change is referred to as buffering. As more acid is added, the buffering effect diminishes as the remainder of the carbonate is converted to bicarbonate. Buffering is the least at pH 8.3, which is indicated by color change from pink to colorless when using the phenolphthalein indicator dye (Figure 3-3). The acid consumed to reach a pH of 8.3 is referred to as carbonate alkalinity (or phenolphthalein alkalinity). For this example the carbonate alkalinity would be 40 mg/L as $CaCO_3$. This example assumes that only carbonate species are present. There are other acid consuming species that would also be measured as phenolphthalein alkalinity, that are discussed later in this chapter.

phenolphthalein

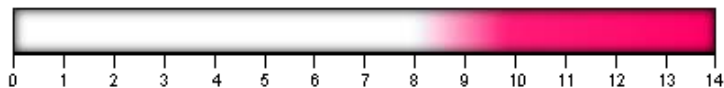


Figure 3-3
Phenolphthalein Indicator Dye Color Change at pH 8.3

Continuing the titration, another buffering zone is encountered around pH 6.3 (the pK_A of bicarbonate and carbonic acid), where bicarbonate is converted to carbonic acid. Continuing the titration to pH 4.3, the bulk of the bicarbonate is converted to carbonic acid. The acid required to lower the pH to 4.3 is referred to as total alkalinity. Total alkalinity is the sum of carbonate plus bicarbonate alkalinity, or methyl orange alkalinity (named after the dye that changes from yellow to orange at pH 4.3; see Figure 3-4). Total alkalinity in this example is 90 mg/L as CaCO_3 . It is not 100 mg/L as CaCO_3 , because at the initial pH (11) about 20 percent of the total carbonate species is present as bicarbonate.

methyl orange



Figure 3-4
Methyl Orange Dye Color Change at pH 4.3

The above analysis ignored the effect of hydroxide in the alkalinity titration. Hydroxide is not present in significant concentrations until the pH approaches 11. When a water sample contains 100 mg/L of total carbonate species at pH 11, the mixture of species is as shown in Figure 3-5. The water in this example contains about 50 mg/L of hydroxide (as CaCO_3).

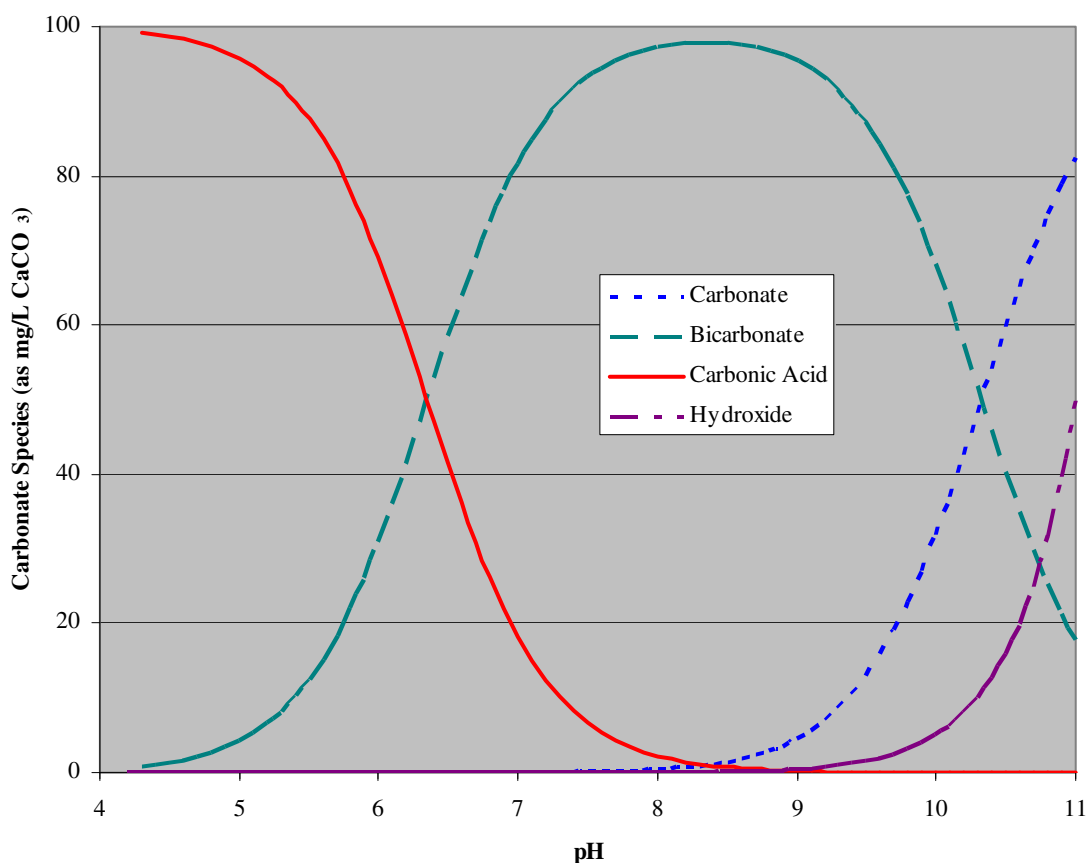
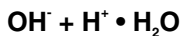


Figure 3-5
Hydroxide and Carbonate Species as a Function of pH (total Carbonates = 100 mg/L)

Titrating this water results in the acid consumption curve as shown in Figure 3-6 (viewed right to left). In this case, carbonate (or phenolphthalein) alkalinity would be 90 mg/L, with 40 mg/L contributed by conversion of carbonate to bicarbonate and 50 mg/L contributed by hydroxide converting to water, according to Equation 3-5.



Equation 3-5

Total (methyl orange) alkalinity would be 140 mg/L as CaCO_3 in this example, as the bicarbonate is converted to carbonic acid.

The above conceptual summary of alkalinity is based on the water being in a closed system, not interacting with the atmosphere. Ash ponds are open to the atmosphere. At low pH carbonic acid will convert to carbon dioxide, and will be lost to the atmosphere, according to Equation 3-6.



Equation 3-6

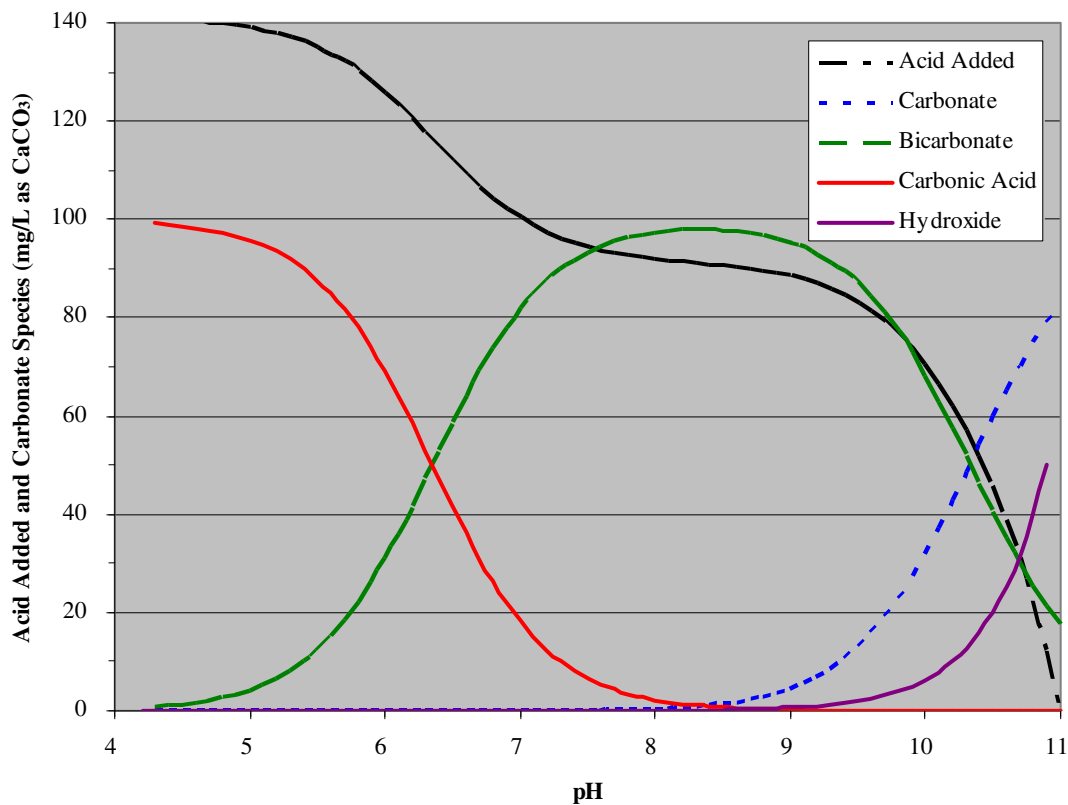


Figure 3-6
Acid Titration (Total Carbonates = 100 mg/L, pH =11)

At alkaline pH, there will be a tendency of CO_2 to be absorbed out of the air forming carbonic acid, which combines with hydroxide (Equation 3-7) or carbonate (Equation 3-8) to form bicarbonate ions.



Note that these reactions do not increase the alkalinity of the water (either hydroxide or carbonate) but rather result in changing the form of the alkalinity from hydroxide or carbonate alkalinity to bicarbonate alkalinity.

Alkalinity can be increased if carbonate or bicarbonate minerals are dissolved in the water (Equations 3-9 and 3-10).

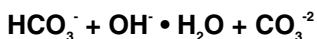


Alkalinity can also be increased by dissolving sodium hydroxide (NaOH) according to Equation 3-11.



Equation 3-11

If carbonic acid is present, this can result in formation of bicarbonate alkalinity (by Equation 3-7) or carbonate by Equation 3-12.



Equation 3-12

The result of this is that to a certain extent, the different forms of alkalinity are interchangeable, depending on the pH and the presence of carbonates. At low pH, carbonates are lost as CO_2 to the atmosphere, and at high pH carbon dioxide will tend to be dissolved out of the atmosphere. Both of these reactions tend to move the pH to neutral (pH 7 to 8) with carbonates principally in the bicarbonate form. At pH less than 7, acid is removed by dissipation of carbonic acid as CO_2 . At pH above 9, carbon dioxide is absorbed from the air, converting hydroxide and carbonate ions to bicarbonate.

Non-Carbonate Alkalinity

Alkalinity is the result of the presence of anions (such as carbonate and bicarbonate) whose pK_A s are between 6 and 10. It can be seen that the species are buffered and react with acid around the pH that is their pK_A . For carbonates, the acid consumption is highest around pH 10.3 for carbonate ions, and 6.3 for bicarbonate ions (see Table 3-1). Anion salts and their pK_A s are listed in Table 3-2. The alkalinity of each species is presented in Table 3-2 as the equivalent mg/L as CaCO_3 .

Table 3-2
Acidity Constants for Ammonia and Other Anions

Anion	Reaction	pK_A	Equivalent Alkalinity (mg/L as CaCO_3)	Resulting from 1 mg/L of:
Acetate	$\text{H}^+ + \text{Ac}^- \rightarrow \text{HAc}$	4.75	0.83	Acetate (HAc)
Pyrophosphate	$\text{H}^+ + \text{H}_2\text{P}_2\text{O}_5^{-2} \rightarrow \text{H}_3\text{P}_2\text{O}_5^-$	5.77	0.81	Phosphorus (P)
Sulfide	$\text{H}^+ + \text{HS}^- \rightarrow \text{H}_2\text{S}$	7.0	1.56	Sulfur (S)
Phosphate	$\text{H}^+ + \text{HPO}_4^{-2} \rightarrow \text{H}_2\text{PO}_4^-$	7.2	1.61	Phosphorus (P)
Pyrophosphate	$\text{H}^+ + \text{H}_3\text{P}_2\text{O}_5^- \rightarrow \text{H}_4\text{P}_2\text{O}_5$	8.22	0.81	Phosphorus (P)
Ammonium	$\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+$	9.2	3.57	Nitrogen (N)
Borate	$\text{H}^+ + \text{H}_2\text{BO}_3^- \rightarrow \text{H}_3\text{BO}_3$	9.2	4.63	Boron (B)
Silicate	$\text{H}^+ + \text{H}_3\text{SiO}_4^- \rightarrow \text{H}_4\text{SiO}_4$	9.5	1.79	Silicon (Si)

These anions buffer an acid when the pH is near their pK_A . They will contribute to alkalinity when the initial pH is near or above these pK_A values. The equivalent alkalinity is that

contributed by these anions when the pH is more than 2 units above these values. When the initial pH is equal to the pK_A , then they contribute only half of their equivalent alkalinity, since at this pH half of the anion is already in the acidic form.

From Table 3-2 we can see that silicate, borate and ammonia can contribute to phenolphthalein alkalinity. Pyrophosphate contributes some, but less than half of the pyrophosphate will be converted to the acid form at the phenolphthalein endpoint (pH 8.3). Pyrophosphate and the other weak acid anions contribute more to methyl orange alkalinity.

Sources of Alkalinity (or Acidity) in Ash Ponds

Coal Combustion

Fly ash and bottom ash are both products of coal combustion. Bottom ash tends to consist of minerals or elements with low volatility that remain as slag after combustion at high temperature in the boiler. Bottom ash tends to consist of inert compounds, contributing neither acidity nor alkalinity to slucewater.

Volatile materials are volatilized and carried up in the combustion gases. As the gases cool, volatile materials condense onto small particles of fly ash that are removed by air pollution control devices. Fly ash can range from very alkaline to very acidic depending on the composition of coal burned and resulting chemical composition of the ash.

In a study of 11 fly ashes from various U.S. power plants, the major components found in fly ash samples were aluminum (Al), iron (Fe) and silicon (Si), with smaller concentrations of calcium (Ca), potassium (K), sodium (Na), titanium (Ti), and sulfur (S) [5]. There are also significant concentrations of magnesium (Mg). Table 3-3 shows the ranges of concentrations of metals in fly ash samples collected from a limited sampling of coal-fired power plants.

The relative composition of these species determines whether the ash will be acidic or alkaline, and the relative strength of the acid or alkalinity. This effect is the result of combustion producing fully or partially oxidized forms of these elements. Ash sluice water pH and alkalinity or acidity is related to calcium, magnesium, iron and sulfur content of the ash, with calcium and magnesium tending to increase alkalinity, and partially oxidized iron (amorphous FeO) and absorbed SO_3 , tending to increase the acidity [5]. The reactions of alkaline earth metals (Ca, K, Na, Mg) found in the first two columns of the periodic table when sluiced with water are shown as Equations 3-13 through 3-16.

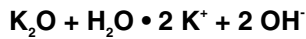
Table 3-3
Selected Chemical Properties of Fly Ash Samples[7]

Parameter	Concentration Range in Fly Ash (mg/kg)
Aluminum	10,800 – 150,000
Iron	10,000 – 190,000
Calcium	2,400 – 30,000
Potassium	1,300 – 102,000
Sodium	220 – 7,500
Titanium	430 – 8,700
Magnesium	980 – 8,600

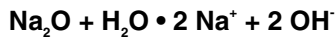
Source: EPRI, 2002[7]



Equation 3-13



Equation 3-14

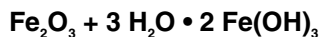


Equation 3-15

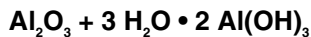


Equation 3-16

As can be seen, the oxides of these elements react with water to produce hydroxide alkalinity (two OH⁻ for each mole of metal). They do this because the solubility of these hydroxide salts is very high. For other metals that are completely oxidized such as the oxides of Fe and Al, the reactions are different, as shown as Equations 3-17 and 3-18. Silicon does not easily react with water.



Equation 3-17



Equation 3-18

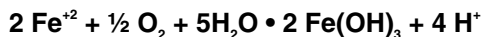
No appreciable hydroxide is produced by these reactions because the hydroxides of iron and aluminum are very insoluble.

Ferric iron salts other than their oxides (such as chlorides or sulfates) may dissolve releasing ferric iron which reacts with water as shown in Equation 3-19.



Equation 3-19

Iron in flyash consists of ferrous and ferric oxides. While ferric oxide does not produce acidity, ferrous does. Dissolved ferrous iron (Fe⁺²) will react with water to generate acid (Equation 3-20).



Equation 3-20

Therefore, iron salts other than their oxides are acidic.

Theis and Wirth [5] found that the property of fly ash which appeared to correlate best with its potential to produce alkalinity was its water-soluble calcium content, while acid-producing potential was best measured by its amorphous (oxalate-extractable) iron content. They introduced a rough rule of thumb for estimating the acidity or alkalinity of a given ash that if the ratio of amorphous iron to water-soluble calcium in an ash is under 3.0, the solution is alkaline and acidic at a ratio above 3.0.

Combustion of coal produces gases that can contribute to the acidity of fly ash. When these “acid” gases mix with water they produce acids. These consist of the oxides of carbon, sulfur and nitrogen, as well as fluoride (Equations 3-21 through 3-24).



Equation 3-21



Equation 3-22



Equation 3-23

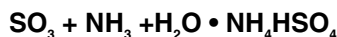


Equation 3-24

Only a small portion of these acid gases are removed in dry fly ash, with sulfur (SO_2 and SO_3) having the most impact on acidity.

SO₃ Mitigation

Ammonia added for SO_3 mitigation tends to increase the acidity of the sluice water. When ammonia is added to the gas phase to control SO_3 , ammonia and SO_3 react to produce ammonium bisulfate (Equation 3-25) a salt particle that is subsequently removed along with fly ash by a baghouse or ESP. When the ash is sluiced with water, the ammonium bisulfate dissociates to ammonium ion and sulfuric acid (Equation 3-26). The result is the generation of acid, although only half of the concentration that SO_3 generates when mixing with water (Equation 3-23), due to the alkaline effect of the ammonia reacting to produce ammonium and hydroxide.

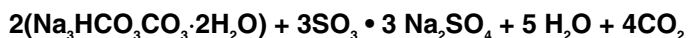


Equation 3-25



Equation 3-26

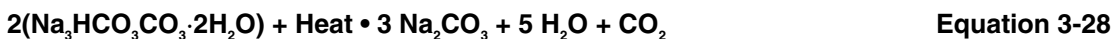
Another chemical used for SO_3 mitigation is trona, or hydrated sodium bicarbonate carbonate, ($\text{Na}_3\text{HCO}_3\text{CO}_3 \cdot 2\text{H}_2\text{O}$), which removes SO_3 from flue gas emissions by Equation 3-27:



Equation 3-27

Excess trona over that consumed in the reaction with SO_3 reacts to produce sodium carbonate by calcination (Equation 3-28).

In SO₃ mitigation, trona is injected upstream of the ESP as a dry sorbent and that which is not consumed by reaction with SO₃ reacts to produce sodium carbonate (Equation 3-28) which is captured by the ESP, with the CO₂ escaping with the flue gas. The sodium carbonate contributes alkalinity to fly ash sluice water (Equation 3-29). One power plant (800 MW unit) indicated trona usage rates of 1,500 to 2,500 pounds per day, which is dependent on the amount of SO₃ produced from coal burning and therefore, dependent on sulfur content of coal.



Ash Conditioning

Ash conditioning, using various chemical treatments, is used at some plants to improve the efficiency of ESP. Two of the primary chemicals used to condition the ash are ammonia and SO₃. When ammonia is used, it will react with SO₃ in the flue gas to create ammonium bisulfate, in the same reactions as happens when ammonia is used for SO₃ mitigation.

If SO₃ is used for ash conditioning, the SO₃ is adsorbed by the fly ash to increase the conductivity of the ash, which improves the efficiency of the ESP. When this ash is sluiced, the water and SO₃ will react to produce sulfuric acid, as shown in Equation 3-23.

FGD Systems

FGD systems using addition of limestone (CaCO₃) create highly buffered FGD blowdown that flows to ash ponds. The addition of limestone during the FGD process results in carbonic acid being added to the FGD wastewater. Carbonic acid dissociates further to bicarbonate in the presence of hydroxide (Equation 3-7) to form alkalinity. As shown in Equations 2-21 to 2-24, acid gases formed during combustion add acidity. These gases are, by design, captured in an FGD. Therefore, FGD systems can contain both acidity and alkalinity. Table 3-4 shows a limited data set of alkalinity and acidity for FGD blowdown from a previous study conducted by EPRI [6].

Table 3-4
Data on Alkalinity, Acidity and pH of FGD Wastewater [6]

Site	Acidity (mg CaCO ₃ /L)	Alkalinity (mg CaCO ₃ /L)	pH
Site E	586	102	6.41
Site P	950	3,200	6.7
Site R	470	5,040	7.1
Site S	70	250	7.1
Site T	274	2,100	7.2
Site U	44.2	75	7.3
Site Y	122	5	5.9
Site Z	15,000	Not Sampled	6.5

Source: EPRI, 2005[6]

A treatability study was conducted at three facilities regarding their FGD wastewater where among several variables, acidity was tested within FGD wastewater (Figure 3-7). The variability in the data between plants indicates the range of acidity values that can be found between facilities.

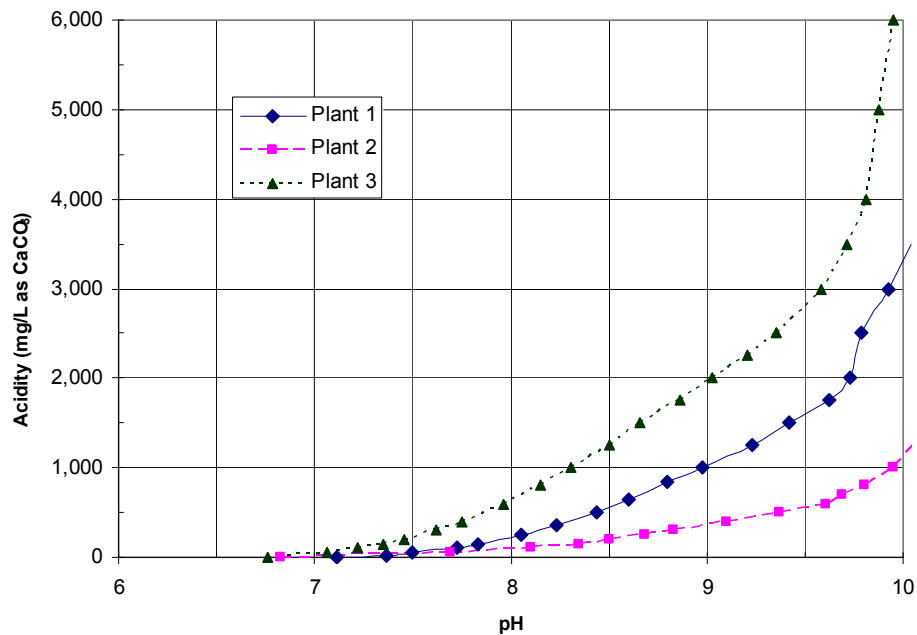


Figure 3-7
Acidity Titration Curves for FGD Wastewater for Three Power Plants

Other Plant Operations Impacting Alkalinity

Other plant operations affect alkalinity of ash ponds principally due to their addition of acidic (which will consume alkalinity) or alkaline waste (which will increase alkalinity). Coal pile and pyrites pile runoff is acidic. Demineralizer regeneration alternates between acidic and alkaline depending on the stage of regeneration, with a resulting short-term significant impact on the combined waste streams. Regeneration tends to be overall acidic, when carbonate de-aeration is used. In addition, limestone piles, gypsum piles, and scrubber solids piles contribute alkalinity to the ash pond influent. Based on a limited data set for scrubber solids runoff, the alkalinity of scrubber solids runoff ranges from 68 to 512 mg/L as CaCO_3 . Overall, due to the low volume and mixing of the acidic and alkaline waste, the overall impact on the pond is minimal.

Caustic Addition to Control Pond Effluent pH

Reactions in ash sluice pond due to ammonia (nitrification and algae growth) generate acids and consume alkalinity. In order to meet effluent pH limits, some plants have had to add sodium hydroxide (caustic soda) to the ponds effluent. Some plants add the caustic to the influent to the pond to maintain conditions conducive to nitrification. One utility added 40,000 to 60,000 gallons of 50% sodium hydroxide to the influent of its ash pond per year to provide for the effects of ammonia addition for ash conditioning and SO_3 mitigation.

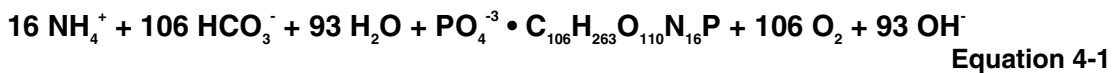
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ROLE OF ALKALINITY IN AMMONIA REMOVAL

This chapter describes the relationship of alkalinity with the ammonia-removal mechanisms algal assimilation and bacterial nitrification/denitrification in an ash pond. The naturally occurring alkalinity of ash ponds varies, depending on the type of coal fired.

Alkalinity in Algal Assimilation of Nitrogen

Algae remove ammonia from ash pond water by incorporating nitrogen into new algae cells (assimilation). Algae are composed principally of carbon, hydrogen, oxygen, nitrogen and phosphorous, in the approximate chemical formula of $C_{106}H_{263}O_{110}N_{16}P$. At neutral pH, algae assimilation of ammonia follows the reaction shown as Equation 4-1.



From this relationship, we can determine that for each mg/L of ammonia-nitrogen ($\text{NH}_4^+\text{-N}$), algae will consume 23.7 mg/L of bicarbonate (HCO_3^-) alkalinity (as CaCO_3). The reaction produces 20.9 mg/L of hydroxide (OH^-) alkalinity (as CaCO_3), so the net result is a reduction of total alkalinity of 2.8 mg/L (as CaCO_3). The reaction also consumes 0.14 mg/L of phosphorus (as P). Algal assimilation may therefore be limited by phosphorus availability within an ash pond. This reaction produces 15.8 mg/L of new algae and 15.1 mg/L of dissolved oxygen (as O).

This reaction has the strange effect of both increasing pH (i.e., increasing hydroxide ions) and decreasing the alkalinity of the ash pond water. This can be understood as loss of bicarbonate reducing the buffering ability of the water such that little hydroxide ion (OH^-) addition is needed to raise the pH.

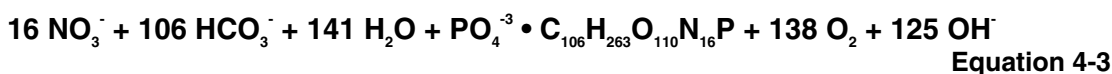
Bicarbonate alkalinity is required for growth of algae and thus bicarbonate alkalinity cannot directly be substituted by hydroxide alkalinity. The bicarbonate can be replaced by a reaction of hydroxide with carbon dioxide (CO_2) which can be dissolved from the atmosphere, as in Equation 4-2.



If bicarbonate alkalinity is not available, then each mg/L of $\text{NH}_4^+\text{-N}$ assimilated will require the transfer of 22.6 mg/L of CO_2 from the atmosphere. If there is CO_2 transfer from the atmosphere, the result of rapid algae growth is depletion of bicarbonate alkalinity and a rise in pH.

Algal assimilation of ammonia also results in significant generation of suspended solids. The assimilation of 2 mg/L of $\text{NH}_4^+\text{-N}$ will generate 32 mg/L of TSS, a number that exceeds typical permits for TSS, if the algae go out with the effluent. If they settle to the bottom of the pond and undergo anaerobic decay, then the trapped nitrogen will be re-released to the water column as ammonia, in approximately the same amount as assimilated. Due to stratification, the release may not affect the upper layers of the pond and the pond discharge until spring or fall overturn, but it can return to the water in subsequent years, reducing the ability of an ash pond to assimilate further ammonia.

Algae preferentially utilize ammonia as their source of nitrogen. If ammonia is not available, they will assimilate nitrate as their source of nitrogen, through the reaction shown as Equation 4-3.



When utilizing nitrate, algae consume 23.7 mg/L of HCO_3^- alkalinity (as CaCO_3) for each mg/L of $\text{NO}_3\text{-N}$ assimilated. The reaction produces 27.9 mg/L of hydroxide alkalinity (as CaCO_3), so the net result is an increase of total alkalinity of 4.2 mg/L (as CaCO_3). The reaction also consumes 0.14 mg/L of phosphorus (as P) and produces 15.8 mg/L of new algae and 19.7 mg/L of dissolved oxygen (as O).

Algae assimilation of ammonia nitrogen consumes alkalinity and raises the pH due to reduction of bicarbonate alkalinity and buffering. Algae assimilation of nitrates results in the same loss of bicarbonate alkalinity but generates more hydroxide alkalinity than the consumption of bicarbonate alkalinity and net alkalinity increases. Both require the same absorption of CO_2 to provide for the carbon needed for algal growth.

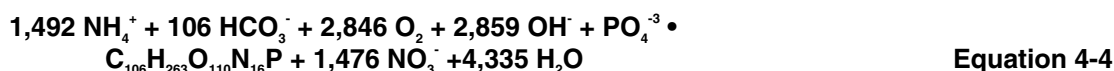
One disadvantage of algal assimilation of nitrate-nitrogen is the release of ammonia during algal decay. Algal assimilation consumes the byproduct of nitrification (discussed further in next chapter) and converts the nitrogen to algal tissue. Subsequent decay of the algae can result in release of ammonia, negating the effects of nitrification on pond ammonia levels. Therefore algal uptake of nitrates should be avoided.

There are significant differences between an ash pond and a natural lake when it comes to algal cycling. In a natural lake, there is considerable movement of carbon (and nitrogen) up the food chain, as algae are consumed by macroinvertebrates, which are then consumed by fish. Ash ponds have a simpler ecology. In addition, the death of organisms within a lake results in a buildup of sediments that are on the order of millimeters or centimeters per year. In ash ponds, ash deposits at a rate of a meter or more per year, trapping detritus, somewhat limiting the re-release of ammonia by subsequent decay.

Alkalinity in Bacterial Nitrification

While algae utilize ammonia for growth, bacteria use ammonia for energy through a process called nitrification. Some 99 percent of the ammonia that is taken up by nitrifying bacteria is oxidized to nitrate and 1 percent is assimilated into cellular tissue for growth. The molecular

formula for bacteria is the same as for algae, and the reaction of oxidation and assimilation can be represented by Equation 4-4. Large numbers are used to avoid working in fractions of molecules.



From this relationship, we can determine that for each mg/L of NH_4^+ -N, nitrifying bacteria will consume 4.36 mg/L of O_2 , 0.25 mg/L of HCO_3^- alkalinity (as CaCO_3) and 6.85 mg/L of OH^- alkalinity (as CaCO_3) or a total alkalinity demand of about 7.1 mg/L (as CaCO_3), producing 0.17 mg/L of bacterial cell mass.

The hydroxide alkalinity can be supplied by HCO_3^- alkalinity as shown by Equation 4-5, but the reaction (Equation 4-4) requires that 0.25 mg/L of alkalinity come from HCO_3^- since this is required to provide the carbon for bacterial growth. These requirements are summarized in Table 4-1.



Table 4-1
Comparison of Requirements for Algal Assimilation and Bacterial Nitrification

	Each mg/L of NH_4^+ -N Assimilated by Algae	Each mg/L of NO_3^- -N Assimilated by Algae	Each mg/L of NH_3 -N Nitrified Requires
Consumes			
HCO_3^- Alkalinity	23.7 mg/L as CaCO_3	23.7 mg/L as CaCO_3	0.25 mg/L as CaCO_3
OH^- Alkalinity	Net Producer	Net Producer	6.85 mg/L as CaCO_3
Total Alkalinity (net)	2.8 mg/L as CaCO_3	Net producer	7.1 mg/L as CaCO_3
Phosphorus	0.14 mg/L as P	0.14 mg/L as P	0.0015 mg/L as P
Dissolved Oxygen	Net Producer	Net Producer	4.4 mg/L as O
Produces			
New Algae Or Bacteria	15.8 mg/L	15.8 mg/L	0.17 mg/L
OH^- Alkalinity	20.9 mg/L as CaCO_3	27.9 mg/L as CaCO_3	Net consumer
Total Alkalinity (net)	Net consumer	4.2 mg/L as CaCO_3	Net consumer
Dissolved Oxygen	15.1 mg/L as O	19.7 mg/L as O	Net consumer

Growth of new bacteria is a result of consumption of this food. The result is that ammonia utilization produces far less growth of new bacteria than that of algae. Each mg of NH_3 -N consumed by bacteria results in the production of 0.17 mg of new bacterial cells. Thus, the demand for carbon and other nutrients is much less.

Summary

Table 4-1 summarizes the impacts of algal assimilation of nitrogen species and nitrification on alkalinity demand or production, dissolved oxygen (DO) demand or production, and production of new cell mass. From this analysis, it can be seen that when ammonia is consumed by algae or bacteria, there is a net consumption of alkalinity. Algae require most of their alkalinity as carbonate species, to provide carbon needed for growth. Since bacteria produce only about 1 percent of the cell growth that algae do, most of the alkalinity for nitrification can be satisfied by hydroxide. If algae assimilate nitrate, they consume carbonate alkalinity in order to provide carbon for growth, generating a net increase in alkalinity by producing more hydroxide alkalinity than the carbonate alkalinity they consume. Algae growth can be limited if the rate of CO₂ absorption from the atmosphere is insufficient to convert the produced hydroxide alkalinity to carbonate alkalinity. Algae assimilation of both nitrogen species produces a net increase in DO, although this can result in oxygen transfer to the atmosphere during the day, and DO depletion at night. Nitrification consumes dissolved oxygen. Both can thus result in complete DO depletion when DO consumption exceeds the pond's capacity to transfer oxygen from the atmosphere.

5

ASH POND MANAGEMENT METHODS FOR EFFECTIVE AMMONIA REMOVAL

As discussed in previous chapters, algal assimilation and bacterial nitrification are the two major mechanisms for removal of ammonia. Management options for promoting algal assimilation and nitrification in ash ponds were discussed in the first volume of this manual. This chapter focuses on encouraging and managing nitrification within an ash pond as it has several advantages over algal assimilation, including:

- Produces significantly lower cell mass yield (approximately 1% of algal assimilation), which results in less impact on effluent TSS.
- Occurs throughout the pond depth, whereas algae can only be produced in the photic zone.
- Algal population fluctuates seasonally within an ash pond and releases ammonia back into the ash pond during seasonal algal die-offs so that there is little net removal of ammonia over the long-term unless algae wash out of the pond (not desirable due to impact on TSS).

The rate of nitrification depends on the growth of nitrifying bacteria. For each pound of ammonia-nitrogen converted to nitrate-nitrogen, 0.17 pounds of nitrifying organism growth must occur. The growth of nitrifiers in pounds per day depends on the mass of nitrifiers present in the pond in pounds times the doubling rate of the nitrifying bacteria (1/day). The doubling rate for nitrifiers is dependent on temperature, pH, DO and ammonia concentration.

In colder temperatures (fall, winter and spring), the growth rate is lower than at warm temperatures (summer). As nitrification occurs, the pH declines due to consumption of alkalinity, decreasing the growth rate. Oxygen is consumed by nitrification. Growth rate declines as DO decreases, particularly if DO is less than 2.0 mg/L. As ammonia is consumed, the lower concentration reduces growth rate also.

The actual growth of nitrifying bacteria also depends on the hydraulic residence time (HRT) of the pond. If the growth rate is less than the rate at which nitrifying bacteria are washed out of the pond (in the effluent), then the population will decline. If ammonia is principally used during the summer ozone season, the result can be a decline of the nitrifying population during the winter. If ammonia is added during the spring, there may be little nitrifying population available to nitrify, until growth increases during the warming months. Hence there may be little ammonia nitrification in April and May and a sudden surge of nitrification in June as the growth rate increases and the bacterial population reaches an effective mass for the available ammonia.

Nitrifier growth rate constant (K) is the product of the growth rate constants as affected by Temperature (K_t), pH (K_p), DO (K_d), and ammonia (K_a) (see Equation 5-1). K_t is referred to as

maximum specific growth rate factor, and has units of 1/day. The other growth rate factors are dimensionless.

$$K = K_t * K_p * K_d * K_a \quad \text{Equation 5-1}$$

HRT is dependent on the effective volume of the pond and flow rate of influent water and rainfall. The effective volume of the pond is reduced from actual volume by the extent of short-circuiting. Thus short-circuiting causes an increase in the portion of the pond's nitrifying organism population that is washed out each day, reducing the inventory of bacteria available for nitrification.

Effect of Temperature on Nitrifier Growth Rate

The growth rate of nitrifying bacteria is principally affected by the temperature of the pond and is shown as Equation 5-2 and Figure 5-1 [8].

$$K_t = 0.47 * 2.71882^{(0.098 * (T - 15))} - 0.05 \quad \text{Equation 5-2}$$

where T is temperature in °C.

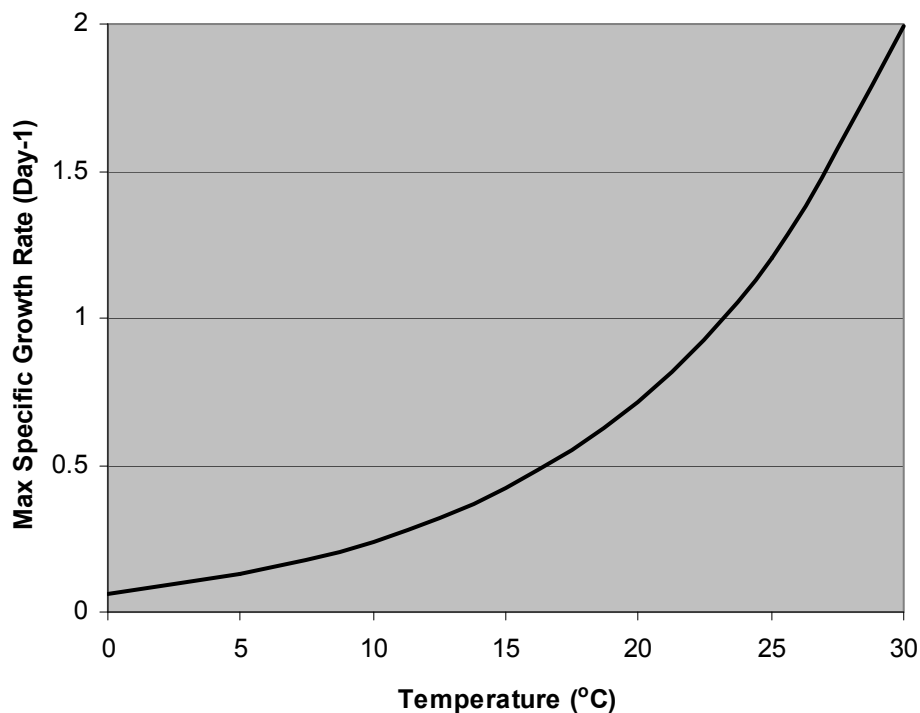


Figure 5-1
Nitrifier Maximum Specific Growth Rate as a Function of Temperature

Effect of pH on Nitrifier Growth Rate

Nitrification is dependent on pH being in a range which is conducive to nitrifier growth. Nitrifier growth is optimal between pH 7 and 9. Outside of this range, growth and rate of nitrification drops off rapidly. Since nitrification generates significant amounts of acid (consuming 7.1 mg/L of alkalinity per mg/L of $\text{NH}_4\text{-N}$ consumed), nitrification is usually limited by a drop in pH. The effect of pH on this growth factor is shown in Figure 5-2 [8].

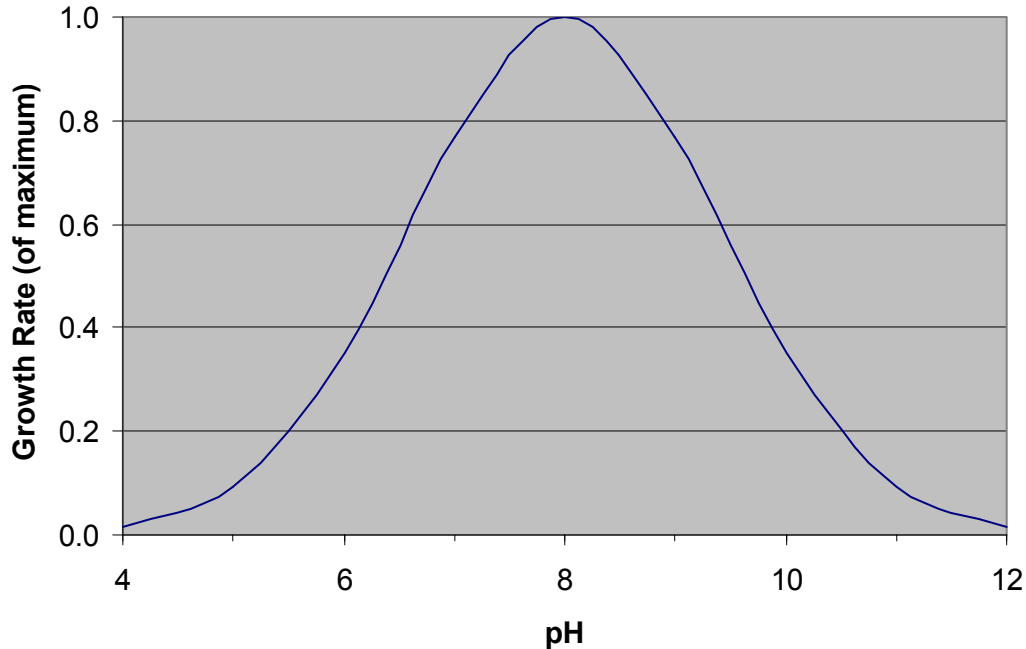


Figure 5-2
pH-Specific Nitrifier Growth Rate as a Function of pH

Effect of Ammonia Concentration on Nitrifier Growth Rate

Relative growth rate of nitrifiers is dependent on the concentration of food (ammonia), by Equation 5-3 and as shown as Figure 5-3 [8].

$$K_a = \text{NH}_4^+ / (T \cdot 0.045 + \text{NH}_4^+)$$

where NH_4^+ is ammonia nitrogen in mg/L
T is temperature in °C.

Equation 5-3

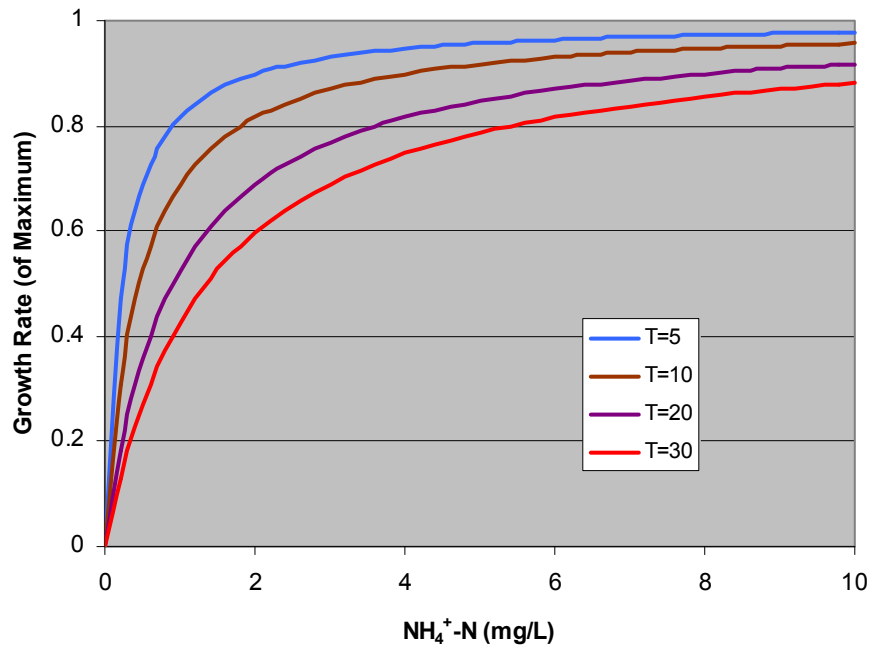


Figure 5-3
Ammonia-Specific Nitrifier Growth Rate as a Function of Ammonia Concentration and Temperature

Effect of Dissolved Oxygen Concentration on Nitrifier Growth Rate

Relative growth rate of nitrifiers is dependent on the concentration of DO, by Equation 5-4, and shown in Figure 5-4 [8].

$$K_d = \text{DO} / (1 + \text{DO})$$

where DO is dissolved oxygen in mg/L.

Equation 5-4

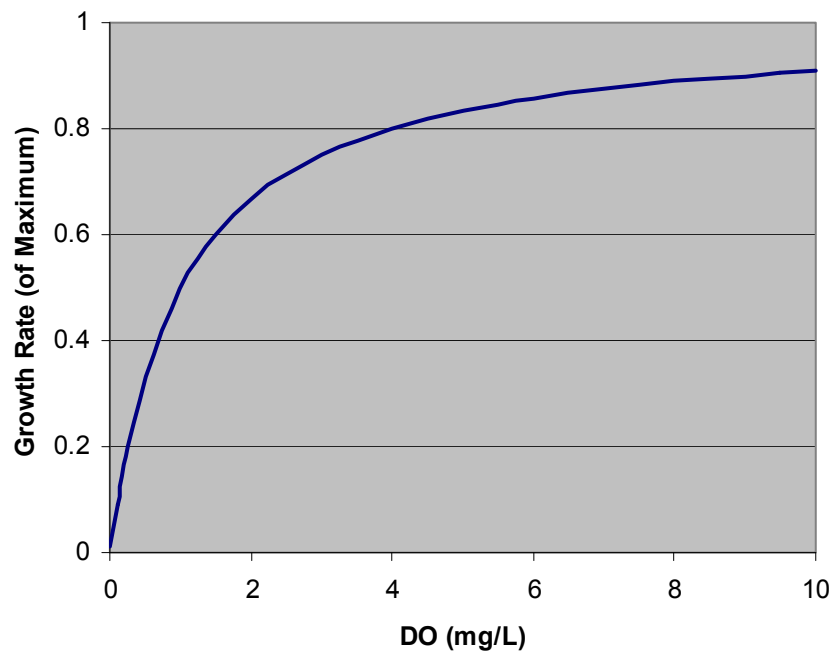


Figure 5-4
DO-Specific Nitrifier Growth Rate as a Function of DO Concentration

The product of these factors (temperature, pH, ammonia concentration, DO concentration) yields the growth rate of nitrifiers.

Field Methods Used for Managing Nitrification

Regulation of nitrification in ash pond is dependent on temperature, pH, ammonia concentration, and DO concentration, as discussed in the previous chapter. In ash ponds, it is not usually feasible to adjust temperature, but an understanding of temperature effects on nitrifier growth and resulting ability to reduce ammonia concentrations is essential to effective control. Short-circuiting can be reduced through design and mixing to prevent thermal stratification. DO can be increased through aeration, and both pH and alkalinity can be adjusted by adding caustic (sodium hydroxide). To make use of these management tools, it is necessary to understand which of the variables is limiting the nitrification reactions. This can be done by evaluating the requirements for nitrification summarized in Table 4-1.

Case Study – Using a Predictive Tool

Management of these key factors is illustrated here using a modeling tool being developed by EPRI for use in managing ammonia removal in ash ponds. The predictive tool performs daily mass balance calculations on factors affecting ammonia in the pond, while tracking nitrogen chemical transformations due to nitrifying bacteria growth. The model covers one year of pond operation, and requires monthly average input values for influent ammonia and alkalinity, wind

speed, pond temperature, pH, and influent flow rate. The model uses the data to provide six months of calculations to reach equilibrium before the year's data is used for analysis. Daily mass balances are performed and summarized as monthly averages.

The predictive tool is utilized in the following examples to show the effects in a hypothetical pond of managing alkalinity through caustic addition, managing residence time through mixing, and managing DO levels through aeration. For each scenario a baseline case was developed in which the factor in question was limiting nitrification (Table 5-1). Pond influent water quality, including ammonia and alkalinity loading, based on an ash pond at a coal-fired power plant where SCR is used for NO_x reduction and ammonia is used for SO₃ mitigation. The base model pond has thermal stratification causing short-circuiting resulting in HRT being reduced by one-half, and inlet and outlet effects resulting in horizontal short-circuiting resulting in reducing HRT by an additional half.

Table 5-1
Model Input Parameters for Case Study

Month	Influent pH	Influent Alkalinity (mg/L CaCO ₃)	Influent NH ₃ (mg/L)	Influent Flow (mgd)	Pond Temp (°C)	Wind Velocity (miles/hour)
January	6.6	29.3	0	7.1	5	5
February	6.6	29.3	0	7.1	10	5
March	6.6	29.3	0	7.1	15	5
April	6.6	29.3	7.1	7.1	19.6	5
May	7.6	41.3	8.0	8.3	20.7	5
June	8.3	44.7	9.9	8.0	26.4	5
July	8.4	42.2	9.5	8.1	28.9	5
August	8.6	54.9	10.8	7.9	28.8	5
September	8.6	54.9	10.8	7.9	20	5
October	8.4	54.9	0	6.6	15	5
November	8.4	54.9	0	6.6	10	5
December	8.4	54.9	0	6.6	5	5

Notes:

Surface Area of Pond = 50 acres

Average Depth of Pond = 15 feet

Total Volume of Pond = 237 million gallons

Adding Caustic to Increase Alkalinity

Nitrification generates acids which consume 7.1 pounds of alkalinity as CaCO₃ per pound of NH₃-N removed. If 2 mg/L influent ammonia as NH₃-N is to be removed, a minimum of 14.2

mg/L of carbonate or hydroxide alkalinity is needed. If a pond has less alkalinity, ammonia removal through nitrification will be limited, due to reduced nitrifier growth at lower pH. The primary option for in-pond management of this alkalinity is caustic (sodium hydroxide) addition. Carbonates are needed by algae for ammonia assimilation. Nitrifier growth requires approximately 1% of the carbonate needed for growth for an equivalent amount of ammonia removal. The algae need the carbon as a building block for growth. The bacteria require large amounts of alkalinity, due to the acid produced during nitrification.

The improvements in nitrification by adding caustic is illustrated in Figure 5-5. In this scenario, ammonia is added for SO₃ mitigation during the ozone season, so as a result little ammonia enters the pond during the winter, with a significant increase in April. As a result, there is a significant rise in pond ammonia in April and May due to the low initial mass of nitrifying organisms and the slow growth during the lower spring temperatures. Ammonia removal improves in June due to the increase in mass of nitrifying organisms based on the warmer month of June. The addition of caustic provides for better removal of ammonia in subsequent months.

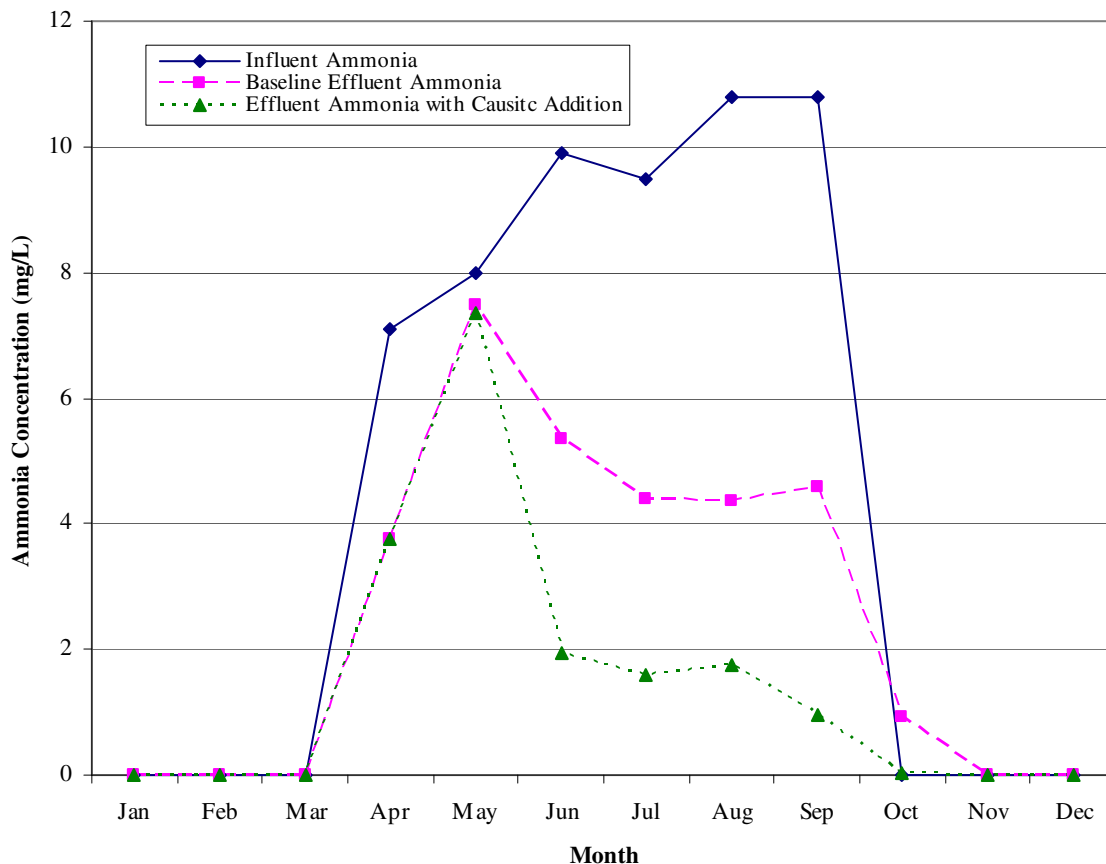


Figure 5-5
Effects of Adding Caustic to Improve Ammonia Removal in Model Ash Pond

Table 5-2 shows the monthly caustic addition for the scenario. These values were derived by using the model to determine addition required to maintain an alkalinity of 50 mg/L in the pond.

Maintaining an alkalinity of 50 mg/L provides a buffer preventing swings in pH, as nitrification produces acid that drives the pH down, limiting bacteria growth which reduces nitrification and results in pH rising to the range where nitrification is favored.

Table 5-2
Caustic Addition Within an Ash Pond for Model Simulation

Caustic Addition (50 percent) (gallons/month)	
January	5,756
February	6,080
March	6,080
April	6,080
May	4,896
June	22,443
July	22,198
August	19,554
September	21,198
October	1,388
November	0
December	0

Mixing to Increase Residence Time

Nitrification requires sufficient residence time so that the nitrifying bacteria are not washed out of the pond faster than they can reproduce. Residence time of a pond is a function of its flow and size, but this is typically very impacted by short-circuiting. Anecdotal evidence suggests that actual residence time can be as little as 10% of the theoretical residence time (size divided by through flow). Short-circuiting can be caused by vertical stratification and lateral short-circuiting.

The hydraulic configuration of the ash pond can have a significant impact on residence time of the pond, due to short-circuiting. As is illustrated in Volume 1 of this manual, the location of the inlet and outlet can affect the lateral short-circuiting, or hydraulic efficiency, of the pond [1]. When the inlet is positioned directly opposite the location of the outlet, short-circuiting of the flow directly across the pond surface is likely, causing a reduction in treatment efficiency. Methods of increasing HRT include baffling ash ponds, by addition of floating baffles or construction of baffles consisting of bottom ash, increasing pond depth with stop logs at the effluent, building a larger pond, and mechanical mixing to break up stratification.

The improvement in ammonia removal by addressing a residence time-limited condition is illustrated in Figure 5-6. In the base case HRT stratification and horizontal short-circuiting

reduce the HRT to 25 percent of that based on pond volume divided by pond effluent flow rate. For the scenario, it is assumed that sufficient mixing is provided to eliminate short-circuiting. In addition, sufficient caustic is added to maintain alkalinity of 50 mg/L. A small amount of mixing energy is required for this, and can be provided without adversely affecting the settling properties of the pond.

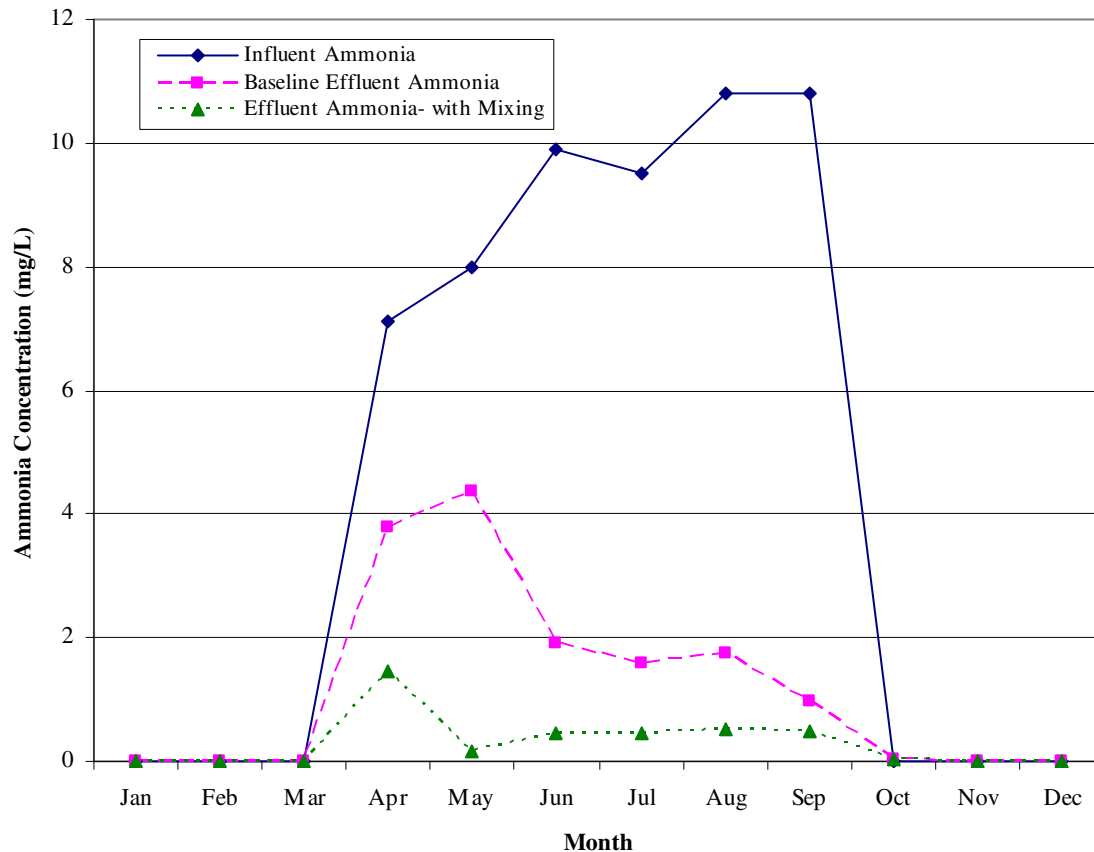


Figure 5-6
Effects on Ammonia Removal of Manipulating Residence Time within an Ash Pond

Increasing Oxygen Transfer

Nitrifiers require 4.57 pounds of oxygen per pound of $\text{NH}_3\text{-N}$ removed. This DO is supplied by oxygen transfer at the surface, predominately driven by wind effects. The model predicts this based on an oxygen transfer model taking into account wind speed, temperature and surface area of the pond.

For large ash ponds, floating aerators can be used for supplying oxygen. Since air is required throughout the pond depth for nitrification, and since there are significant benefits of mixing, it is recommended that mixing aerators are used to draw water from the lower reaches of the pond (which likely have lower DO due to lack of access to surface air), and add DO. Floating aerators

typically provide between 2.5 to 3.0 lbs of oxygen per hour per horsepower (hp). Hence a rough estimate of aeration capacity would be 8 hp of aerators per hundred pounds of ammonia nitrogen to be nitrified per day.

The improvements in ammonia removal by addressing an oxygen-limited condition is illustrated in Figure 5-7. The baseline scenario was modeled by limiting oxygen transfer by reducing wind velocity to zero for this scenario. The theoretical improvement reflects the improvement in ammonia removal achieved by increasing the oxygen in the pond to near saturated conditions (approximately 80% saturated DO).

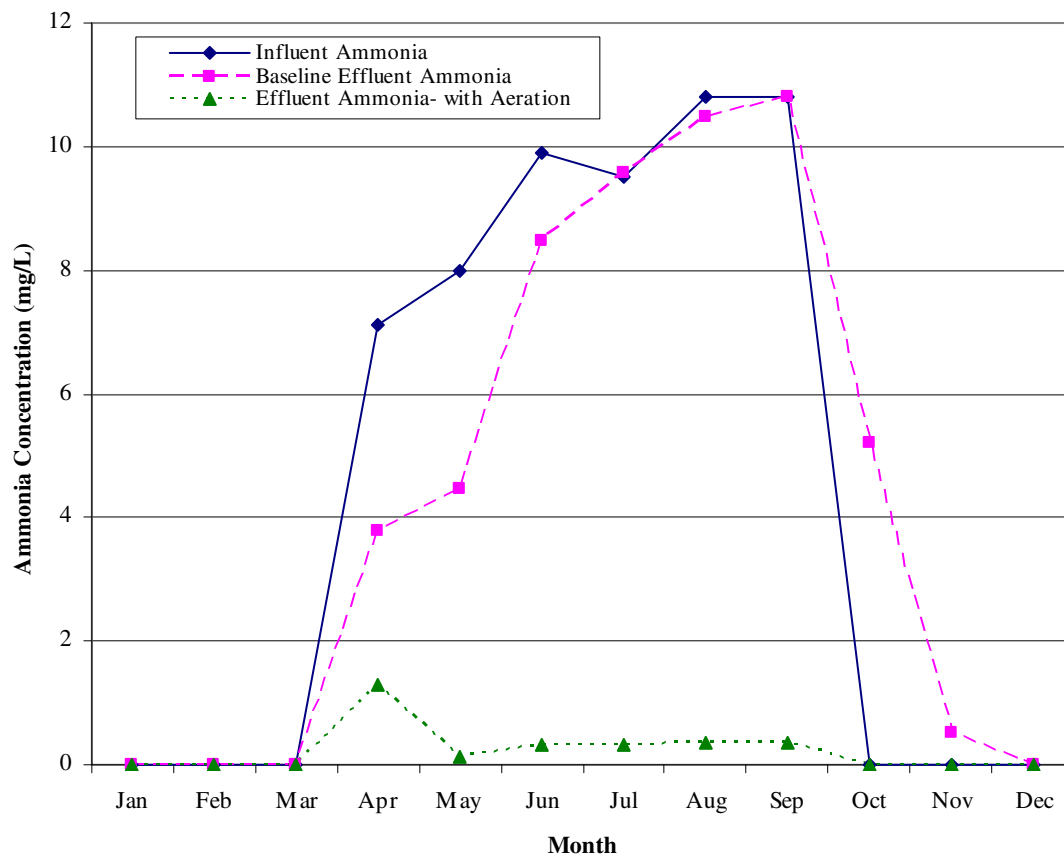


Figure 5-7
Effects on Ammonia Removal of Manipulating Dissolved Oxygen Levels by Aeration within an Ash Pond

Model Benefits

As can be seen in these examples, the model is useful in predicting performance of ash ponds for prediction of ammonia in the effluent based on nitrification. It also assists in predicting effects of manipulating the pond conditions to improve removal, and determining the optimum addition of aeration or caustic to optimize removal efficiency.

6

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